INTERMEDIATE CHEMISTRY

Elements of Inorganic and Organic Chemistry

For Intermediate, Pre-university, Higher Secondary, Senior Cambridge
and Pre-professional, such as Pre-medical and Pre-engineering, courses

BY

P. K. DUTT

Professor of Chemistry,
Presidency College, Calcutta
and
Post-Graduate Lecturer in Inorganic Chemistry,
Calcutta University.

UTTARPARA
JAIKRISHNA PUBLIC LIBRARY.

SCIENCE BOOK AGENCY
P-133B, LAKE TERRACE
CALCUTTA-29

1912

Published by
SISIR KUMAR DATTA
14/17A, Golf Club Road,
Calcutta-33

(All rights reserved by the publisher)

PRICE : Rupees ten only.

Printed by
PHANI BHUSAN ROY,
THE PRABARTAK PRINTING AND HALFTONE LTD.,
/3 [illegible]pin Behary Ganguly Street, CALCUTTA—12.

PREFACE

ermediate Chemistry is a text-book of elements of inorganic ganic Chemistry for *Intermediate, Pre-university, Higher Secondary, Cambridge and Pre-professional, such as Pre-medical and Pre-engineering,* . It fully covers the requirements of examinations of different sities and Boards. It is believed that the book would be useful to the beginners as an introduction of the science of ry.

the presentation and general arrangement of the subject the has been largely guided by his experience as a teacher of try for nearly three decades. In view of the continual advances eaching of Chemistry, the presentation of the subject matter en very carefully brought into line with recent practice as possible—the fundamentals have been very clearly explained chemistry ceases to be mechanical as was the hitherto mistaken

significance of chemical equations has been thoroughly ded by the introduction of *partial equations* in the book. ical problems have been carefully graded and many easier s have been incorporated. Select and up-to-date questions iversity papers have been added at the end of each chapter.

ial emphasis has been laid throughout on the applied aspect istry so that the students from the early years of its study may e science and not merely *wear* it.

facturing processes have been described in the light of counts available in our country.

ncere thanks are due to numerous friends and teachers for help in the preparation of the text. My thanks are also Mahim Chandra Biswas, Manager, Prabartak Printing and Ltd., and to Sri Sukomal Dutt, M. Com., for their ling co-operation in the quick production of the book.

take this opportunity of expressing my indebtedness to Sarkar, D.Sc., F.N.I., Director, Technological Research es, Indian Central Jute Committee for his helpful sympathy advice.

S. DUTTA

CONTENTS—Part I
(Inorganic Chemistry)
General Chemistry

[illegible]ATER		PAGE
	Preface	iii
I	Science and Chemistry	1
II	Fundamental concepts	8
III	Symbol, formulae and equations	24
IV	Acids, bases and salts	36
V	Common laboratory processes	39
VI	Physical properties of gases	64
VII	The laws of stoichiometry and atomic theory	75
VIII	Chemical equivalents and atomic weights	90
IX	Molecular weights	105
	Osmosis and osmotic pressure	108
X	Law of mass action	115
XI	Electrolytes and electrolysis	120
XII	Thermochemistry	142
XIII	Catalysis	144
XIV	Colloidal solutions	146
XV	The structure of matter	152
	Radioactivity	160
XVI	Periodic classification of elements	161

Non-metals

XVII	Oxygen, hydrogen and water :	
	Oxygen	172
	Hydrogen	180
	Water	188
VIII	Ozone and hydrogen peroxide :	
	Ozone	202
	Oxidation and reduction	207
	Hydrogen peroxide	212
XIX	Nitrogen and the atmosphere :	
	Nitrogen	219
	The atmosphere	222
XX	Compounds of nitrogen :	
	Ammonia	228
	Oxides of nitrogen	239
	Nitrous acid	246
	Nitric acid	248
XXI	The halogens :	
	Fluorine	258
	Hydrofluoric acid	261
	Chlorine	262
	Bromine	267
	Iodine	270

CHAPTER		PAGE
	Hydrochloric acid	273
	Oxides and oxyacids of chlorine	280
	Oxides and oxyacids of bromine and iodine	286
XXII	Sulphur and its compounds :	
	Sulphur	295
	Hydrogen sulphide	300
	Sulphur dioxide	303
	Sulphuric acid	307
XIII	Carbon and its compounds :	
	Carbon	317
	Carbon dioxide	322
	Carbon monoxide	327
	Hydrocarbons	330
	Combustion	346
XXIV	Phosphorus and its compounds :	
	Phosphorus	353
	Phosphine	35[illegible]
	Arsenic, antimony and bismuth ...	36[illegible]
XXV	Boron and silicon :	
	Boron	37[illegible]
	Silicon	37[illegible]

Metals

CHAPTER		PAGE
XXVI	Metals and metallic compounds	385
XXVII	The alkali metals :	
	Sodium	395
	Potassium	407
XXVIII	The alkaline earth metals :	
	Magnesium	412
	Calcium	415
	Strontium and barium	41[illegible]
XXIX	Zinc, cadmium and mercury :	
	Zinc	421
	Cadmium	427
	Mercury	428
XXX	Aluminium	4[illegible]3
XXXI	Tin and lead :	
	Tin	4[illegible]1
	Lead	4[illegible]6
XXXII	The coinage metals :	
	Copper	453
	Silver	461
	Gold	467
XXXIII	Iron, cobalt and nickel :	
	Iron	
	Cobalt and nickel	
XXXIV	Chromium and manganese	
XXXV	The inert gases	

Chemical problems

CHAPTER PAGE
XXXVI Chemical calculations 497
Percentage composition 501
Chemical equations 505
Eudiometry 514
Acidimetry and alkalimetry 521
Oxidation reactions and iodometry ... 538

Appendix :

Balancing redox equations 540
Measurements, etc. 543
Index 545

CONTENTS—Part II
(Organic Chemistry)

I General theory ... ...

Aliphatic compounds

II Paraffins 7
III Unsaturated hydrocarbons 11
Olefines 12
Acetylenes 15
IV Halogen derivatives of paraffins 17
V Alcohols 23
VI Ethers 30
VII Aldehydes and ketones 33
VIII Fatty acids 42
IX Derivatives of acids 49
X Oils, fats and glycerol 55
XI Amines 60
XII Dibasic acids 62
XIII Hydroxy acids 66
XIV Carbohydrates 73

Aromatic compounds

XV ~~Benzene and its~~ homologues 81
XVI Halogen derivatives 86
XVII Nitrobenzene 87
XVIII Aniline 88
XIX Phenols 92
XX Alcohols, aldehydes and acids 95
XXI Food and nutrition 99
XXII Organic manipulation 103
XXIII Analysis of organic compounds :
Qualitative analysis 109
Quantitative analysis 111
XXIV Empirical and molecular formula 117
Questions 121
Index 551

International Atomic Weights, 1954.

Name	Symbol	At. no.	At. wt.*
Actinium	Ac	89	227
Aluminium	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.76
Argon	A	18	39.941
Arsenic	As	33	74.91
Astatine	At	85	(210)
Barium	Ba	56	137.36
Berkelium	Bk	97	(245)
Beryllium	Be	4	9.013
Bismuth	Bi	83	209.00
Boron	B	5	10.82
Bromine	Br	35	79.916
Cadium	Cd	48	112.41
Calcium	Ca	20	40.08
Californium	Cf	98	(246)
Carbon	C	6	12.010
Cerium	Ce	58	140.13
Cesium	Cs	55	132.91
Chlorine	Cl	17	35.457
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Columbium : see Niobium			
Copper	Cu	29	63.54
Curium	Cm	96	(243)
Dysprosium	Dy	66	162.46
Erbium	Er	68	167.2
Europium	Eu	63	152.0
Fluorine	F	9	19.00
Francium	Fr	87	(223)
Gadolinium	Gd	64	156.9
Gallium	Ga	31	69.72
Germanium	Ge	32	72.60
Gold	Au	79	197.2
Hafnium	Hf	72	178.6
Helium	He	2	4.003
Holmium	Ho	67	164.94
Hydrogen	H	1	1.008
Indium	In	49	114.76
Iodine	I	53	126.91
Iridium	Ir	77	193.1
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.92
Lead	Pb	82	207.21
Lithium	Li	3	6.940
Lutecium	Lu	71	174.99
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.93
Mercury	Hg	80	200.61
Molybdenum	Mo	42	95.95
Neodymium	Nd	60	144.27
Neptunium	Np	93	(237)
Neon	Ne	10	20.183
Nickel	Ni	28	58.69
Niobium	Nb	41	92.91
Nitrogen	N	7	14.008
Osmium	Os	76	190.2
Oxygen	O	8	16.0000
Palladium	Pd	46	106.7
Phosphorus	P	15	30.975
Platinum	Pt	78	195.23
Plutonium	Pu	94	(242)
Polonium	Po	84	210
Potassium	K	19	39.100
Praseodymium	Pr	59	140.92
Promethium	Pm	61	(145)
Protoactinium	Pa	91	231
Radium	Ra	88	226.05
Radon	Rn	86	222
Rhenium	Re	75	186.31
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.7
Samarium	Sm	62	150.43
Scandium	Sc	21	44.96
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.880
Sodium	Na	11	22.997
Strontium	Sr	38	87.63
Sulphur	S	16	32.066
Tantalum	Ta	73	180.88
Technetium	Tc	43	(99)
Tellurium	Te	52	127.61
Terbium	Tb	65	159.2
Thallium	Tl	81	204.39
Thorium	Th	90	232.12
Thulium	Tm	69	169.4
Tin	Sn	50	118.70
Titanium	Ti	22	47.90
Tungsten	W	74	183.92
Uranium	U	92	238.07
Vanadium	V	23	50.95
Wolfram : see Tungsten			
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

---

* A value given in a bracket denotes the mass number of the most stable isotope.

INTERMEDIATE CHEMISTRY

Elements of Inorganic and Organic Chemistry

INORGANIC CHEMISTRY

I

SCIENCE AND CHEMISTRY

Science.—Science stands for the sum-total of human knowledge and it extends over the entire realm of nature. All natural phenomena follow one another in an endless chain of cause and effect. Science attempts to seek a unity in the diversity of nature. It, therefore, aims at devising a model of the universe that will explain all that goes on in it, and will also predict its future behaviour. Science gathers facts by observing events in the universe and by collecting results of experiments. Collected in books and in the minds of men, they make the knowledge of our civilisation, but not necessarily **science.** Science is an organised body of facts which have been interrelated and generalised into a system.

Antoine Laurent Lavoisier (1743-94)

FIG. 1

The study of science begins by collecting and comparing facts. When experiments and observations of the same kind yield similar results, it becomes possible to combine them together into general statements, called **laws.** Natural laws may either be discovered by the correlation of experimentally established facts or by making an intuitive guess at some general principles, as to the cause of natural phenomena. Such a speculation is called a **hypothesis.** A hypothesis must not only explain the known facts, i.e., it must be in conformity with the laws, but also predict the discovery of new facts. But when experiments fail to confirm its predictions, the hypothesis is rejected and a new one framed and similarly tested. If the hypothesis survives these tests, it becomes a theory and makes an integral part of the fabric of natural science. A theory in its turn is put to similar tests of predictions and experimental verification. When every fresh finding confirms the theory and proves its truth to the hilt and beyond all reasonable doubt, it is dignified by the name of a **law**; but if found wanting, it must either be discarded or modified. A scientific theory is always provisional, but none the less, it stimulates research. Scientific discoveries are but the results of intensive search for new facts and laws, guided by the intelligent use of theories.

Science is a coherent whole and touches all human interest. Natural science has been conveniently divided into different branches for the purpose of study. *Physics* and *Chemistry* belong to the group of physical science which deals with matter and energy without any reference to life. *Botany* and *zoology*, on the other hand, are different branches of biological science which is concerned with living things and phenomena relating to life process. Other notable departments of natural science are *Astronomy*, *Geology*, *Geography*, *Physiology*, and so forth.

Chemistry.—The term chemistry is derived from the word 'chemia', the ancient name of Egypt, which signified a 'divine art' that was highly developed and much practised in the country in the first few centuries of the Christian era. Chemistry as a science is but a recent growth. *The science of chemistry is the study of matter, its properties, composition, and the changes it undergoes.* It is concerned not only with changes in the composition of matter, but also with the gain or loss of energy which accompanies the changes, and the natural laws which govern these changes.

"The aim of chemistry is to separate the different substances that enter into the composition of bodies; to examine each of them apart; to discover their properties and relations; to decompose those very substances, if possible; to compare them together and to combine them with others; to reunite them into one body as to produce the original compound with all its properties; or even to produce new compounds that never existed amongst the works of nature."

The chief departments of chemistry are three: (a) **Physical chemistry,** (b) **Inorganic chemistry,** and (c) **Organic chemistry.**

Physical Chemistry, which takes note of the scientific laws and principles that govern transformations of matter. Physical chemistry in its turn is studied under different headings, viz., *thermochemistry*, *electrochemistry*, *photochemistry* dealing with chemical reactions caused by radiation, *nuclear chemistry*, *magneto chemistry*, and *colloid chemistry*, etc.

Inorganic Chemistry, which is mainly concerned with mineral matter and deals with materials that do not contain carbon. Study of various minerals, metals and non-metals, acids, bases and salts, come under the scope of inorganic chemistry. **Mineral Chemistry** is an important section of inorganic chemistry. **Geo-chemistry** is another important section.

Organic Chemistry, which is the chemistry of carbon compounds and mainly deals with products of plant and animal origin, viz., proteins, fats and oils, carbohydrates, alkaloids, hormones and vitamins, dyes, etc. ; each of the items forms an important branch of organic chemistry. Drugs are also studied under organic chemistry. Several simple carbon compounds like carbon dioxide, carbon disulphide, etc., are however, treated in both organic and inorganic chemistry. Besides, there are other ramifications of the science of chemistry. **Biochemistry** deals with the chemistry of living organisms ; a comparatively young science, it has made phenomenal strides in recent years. Vitamins and hormones which are the two master keys to the life processes come under the realms of biochemistry. Antibiotics, and food and nutritional problems are also studied under this head. As an aid to medicine [**pharmaceutical chemistry**] developed into a special branch from very ancient times. Detection and estimation of chemical substances form an integral part of the study of chemistry ; the branch of **analytical chemistry** fulfils this function. **Applied chemistry** is another very important special branch of chemistry, and is concerned with the chemistry and technique of the industrial processes. But for applied chemistry many of the chemicals of everyday use would have remained mere test tube curiosities. Cement, glass and ceramics, fuels and furnaces, metals and alloys, acids and alkalis, fertilisers, dyes and drugs, paints and pigments, pulp and paper, plastics, pesticides, petroleum and fermentation chemicals, fibres, rubber, oils and fats, sugar, water-conditioning, explosives and abrasives are some of the pointers in the ever-expanding front of chemical technology. **High polymer chemistry,** i.e., chemistry of macromolecules, popularly called **plastics,** is another branch of chemistry which has lately come into prominence. **Soil chemistry** is also studied as a special branch.

Chemistry and the community.—The science of chemistry has contributed much to improve the life of men. Pottery, porcelain, paper, glass, cement, oils, petrol, paints, varnishes, dyes, plastics, fibres, drugs, metals, alloys, etc., which now form the integral parts of modern life, are the gifts of chemical science. Commonplace raw materials have been worked by chemists into many useful things of everyday life. Wood, for example, has been transformed into paper, sugar, artificial silk, mercerised cotton and celluloid. It is very often found that waste materials have been profitably utilised by chemists. Coaltar, for example, has been made to yield many brilliant dyes, potent drugs, durable plastics, sweet perfumes, nylon, and saccharin.

New discoveries are always being made and the new applications of old discoveries found for the benefit of the people. The wonder drugs *penicillin*, *chloromycetin* and *streptomycin* are the rich harvests of unremitting chemical research. *Sulpha drugs* are well-known aids in medicine. Planned synthetic chemistry has lifted the veil of nature and has made new substances to order. Some of the milestones are the syntheses of indigo, camphor, cocaine, plant pigments and the red colouring matter of blood. Synthetic rubber and petrol are produced in plenty. Chemistry applied is pelf and power acquired. The science of chemistry goes a great way to build a sound national economy by proper utilisation of natural resources of a country. It has undoubtedly considerably helped the community to shift from savagery to civilisation. Chemistry supplies the needs of our ever advancing civilisation.

Chemistry has also greatly helped the development of other sciences such as physiology, geology and agriculture. Digestion of food is a chemical change. Chemical knowledge has made the examination of milk, soil and water possible. It has also helped the development of fertilisers, insecticides, fungicides and germicides. Chemistry also greatly help in the detection of crimes and revelation of frauds. Improper exploitation of chemical discoveries has often made much harm to people—adulteration of food and medicine by anti-social elements, and fraudulent practice of replacement of genuine things by artificial imitations call for constant vigilance and expert chemical knowledge. But its direct uses in life apart, its educative value is no less important. The methods of chemistry help us to cultivate the scientific attitude of mind and discipline in life.

Chemistry also plays a very vital role in war. High explosives incendiary bombs, rocket fuels, smoke screens and poison gases are some of the dreadful gifts of chemistry to the warring nations. *Chemical warfare* involving use of poison gases was started by the Germans in the last Great War with the release of 600,000 lbs. of chlorine along a 2-mile front against an unprotected enemy. *Tear gases,* also called lachrymators, powerful vesicants like *mustard gas* which causes serious blisters on the skin, and such poison gases which injure the lungs or the eyes or cause sneezing, nausea, and other physical disabilities were freely used as weapons of chemical warfare. But the *atom bomb*, the monster babe of the second global war, beats all records of monostrosity ; its horrors beggar all descriptions. It carried fire and destruction to Japan. Still deadlier *hydrogen-bombs* have been produced.

Chemical power of a nation is an index of its military prowess. Exigencies of war have often led to great chemical discoveries. Chemistry is, however, by no means, a science of destruction and scourage to humanity. Whether a curse or blessing, it depends upon the uses to which it is put. "Science in itself is ethically neutral. It confers power, but for evil just as much as for good". Many wonderful engineering feats, for example, have been performed with the help of high explosives—explosives are the most powerful slaves that man has learned to employ. Atomic energy would prove a blessing to mankind, if properly harnessed and exploited to generate power. Atomic reactors have already been put into action in many countries for the peaceful exploitation of power.

History of Chemistry.—The beginnings of chemistry are lost in the mists of antiquity. No one can tell precisely when and how it began. But there is no doubt that the origin of chemistry lies in the technical arts and crafts of primitive civilisations. The hoary civilisations of ancient Egypt, India, China, Sumer, Assyria and Babylonia—all made positive contributions to the science of chemistry. The art of painting and dyeing, the preparation of medicinal remedies and perfumes the manufacture of glass and porcelain, extraction of common metals like gold, silver, copper and iron for example, formed an important feature of even very primitive civilisation. Of all the early civilised people, the Egyptians were a practical race and developed the art of chemistry greatly, and had great traditions in the working of metals and glass, and in the dyeing of fabrics. They were also past masters in the art of embalming. The Greek philosphers, on the other hand, who were no practical chemists, made speculations as to the physical background of the universe. **Aristotle's** (384-322 B.C.) theory of four elements, viz., **fire, air, earth,** and **water** which represented but four fundamental qualities only, was one of the earliest attempts to explain the nature of matter. All substances were supposed to be made up of a primitive matter or *prima materia* which could produce different forms of matter when the four elements were impressed upon it. The different forms could, however, be transformed into one another by the proper working of the four elements. The germ of the theory of transmutation of elements was, therefore, contained in the theory of four elements. Another Greek school of thought, headed by **Demokritos and Leukippos,** speculated about the units of composition of matter, which we now call atoms. Speculations of comparable nature as to the structure of matter were also traceable in the writings of the ancient Indians. There sprang up, for example, in India, prior to Aristotle, a system of philosophy which assumed the existence of five elements viz., *khiti* (earth), *apas* (water), *tejas* (fire), *marut* (air), and *byoma* (ether-space). The atomic theory was conceived very early in our land, much before the Christian era, by the Hindu philosopher **Kanad.**

The vague metaphysical speculations of the ancients let alone, there are three distinct stages in the development of the science of chemistry ; they are the periods of (i) **Alchemy** up to the 15th century, (ii) **Iatrochemistry** from the 16th century up to the middle of the 17th century, and (iii) **Scientific chemistry** when the study of chemistry was taken up for its own sake. It is generally agreed that chemistry had its origin in the Egyptain city of Alexandria which was a great citadel of science and culture in the beginning of the Christian era. The fusion of the practical ideas of the Egyptians and the philosophical speculations of the Greeks gave birth to the idea of **transmutation of elements,** viz., the '*divine art*' of making gold, called **Alchemy.** Alchemy was a sort of admixture of science and religion, black magic, superstition, and obscure mysticism. The alchemists laboured under the peculiar notion of transforming the base metals into gold through the agency of the so-called **philosopher's stone** for which they searched in vain. The era of alchemy was marked by vigorous searches by the alchemists for the discovery of the **philosopher's stone** and the **universal solvent for transmutation of base metals into gold.** Many fraudulent processes were described in alchemical literature for the falsification of precious metals. But their barren endeavours led to the invention of many technique which we still use, viz., distillation, sublimation, digestion, and filtration, etc.

So matters stood until the seventh century, when the Arabs overran Egypt and the manuscripts on alchemy gradually passed into Arabia. Alchemy under the Arabs slowly percolated into Europe in the 12th and 13th centuries mostly through Spain which was then the confluence of the Arabic and European culture. The names of **Roger Bacon** and the famous Arabian alchemist **Geber** stand out very prominently in this period. The Arabian alchemists taught that metals were composed of mercury and sulphur. The practice of alchemy soon rose to a position of importance in Europe. But with time it degenerated into a trickery and fell into disrepute. Alchemy in India made parallel and independent developments under the Tantric school of thoughts in the 8th century. The period of alchemy ended with the closing of the 15th century.

With the decline of alchemy, there arose the school of **iatrochemists** i.e., *medical chemists*, whose aim was to discover **elixir of life** which would cure all diseases and confer perpetual youth on man. The founder of this school was **Paracelsus** (1493-1541 A.D.) who declared the preparation of medicine to be the only aim of chemistry. Chemistry was thus made a handmaid to medicine. Paracelsus expounded the theory that the real elements are *mercury*, *sulphur*, and *salt.* Iatrochemistry made phenomenal progress in ancient India. Vegetable remedies were known to the ancient Indians even long before the Christian era. *Charaka*, *Susruta*, *Vrinda*, *Chakrapani* and *Nagarjuna* were the leading iatro-chemists of our country.

Renaissance in Europe in the sixteenth and seventeenth centuries gave birth to a new spirit of enquiry which gave impetus to the pursuit of science for its own sake and not for making gold or medicine. The founder of modern science is **Francis Bacon** (1561-1626) who laid stress on the inductive method of studying science. His writings are amongst the greatest contributions to human thought since the time of the Greeks.

The era of scientific chemistry began with **Robert Boyle** (fig. 2) (1627-91) who by clearly distinguishing elements 'as things which cannot be decomposed further' in his great book *Sceptical Chymist* (1661) overthrew the Aristotelian theory of four elements which held the field for nearly two thousand years, and also successfully refuted the doctrine of alchemical elements. The century after Boyle's death saw the rise and fall of the famous but incorrect **Theory of Phlogiston,** elaborated by two German scientists **Becher** and **Stahl,** which asserted that all combustion was but release of phlogiston. Calcination of metals into calx was supposed to be due to the escape of phlogiston :

Robert Boyle (1627-91)

FIG. 2

Metal − phlogiston = calx of metal.

The calx, when treated with a carbon which was regarded to be rich in phlogiston, gave back the metal. The theory had therefore, the merit of explaining many facts of chemistry at that time but it overlooked the obvious function of air in combustion.

Towards the latter part of the eighteenth century our knowledge of chemical substances was largely extended. The most notable discovery of the time was the gaseous element oxygen. It was independently discovered by the Swedish pharmacist **Scheele** and the English clergyman **Priestley** and by a curious coincidence in the same year 1774. At about the same time **Cavendish** carried out his famous researches on the composition of water. But confirmed believers in phlogiston, they could hardly realise the importance of their great discoveries.

Towards the end of the eighteenth century the French savant (fig. 1) **Antoine Laurent Lavoisier** (1743-94) set himself to the discovery of the cause of calcination of metals, and was quick in realising the importance of the discovery of oxygen in his unfinished work. The convincing experiments of Lavoisier proved beyond doubt that the calcination of metals was due to the absorption of oxygen from air which made the calx heavier. The loss of phlogiston would have made the body lighter after calcination, which was not a fact. This led to the overthrow of the theory of phlogiston. None the less, the discredited and abandoned theory held sway over the contemporary leading chemists for a long time, the overwhelming evidence to the contrary notwithstanding. Lavoisier also introduced the use of balance in the domain of chemistry and with its help discovered in the year 1774 the *principle of indestructibility of matter* which is the very basis of modern chemistry. He is therefore, very rightly called the maker of modern chemistry and it is often claimed that '*chemistry is a French science and its founder is Lavoisier of immortal fame.*'

The next landmark in the evolution of chemistry was the publication of the atomic theory by **John Dalton** in the year 1803. The discovery of the law of gaseous volumes by **Gay Lussac** in 1808 led to a direct conflict with Dalton's atomic theory, which resulted in the enunciation of the famous hypothesis by the Italian scientist **Avogadro** in the year 1811 ; this is referred to as Avogadro's hypothesis. The hypothesis was unfortunately left unappreciated till 1856 when **Cannizzaro,** a pupil and a countryman of Avogadro made it an indispensable guide in the subsequent development of chemistry. Shortly after the announcement of the atomic theory the famous Swedish chemist **Berzelius** to whom was due the present system of chemical symbols, set out to obtain the first table of atomic weights of elements. This was a busy period of determining the atomic weights which was given a further stimulus by the publication of **Prout's hypothesis** in 1815 that 'the atomic weights of elements are the whole multiples of that of hydrogen.' This attractive hypothesis, though disproved by the classical investigations of the Belgian chemist **Stas** (1813-91), gave powerful stimulus to experimental researches. The publication of the 'periodic table of elements' by the celebrated Russian chemist **Mendeleef** (1834-1907) in 1869 led to renewed experimental activities in the domain of chemistry. Finally, the determination of the atomic weights by T. W. Richards (1867-1928) on whom the mantle of Stas had fallen, was universally regarded as the masterpieces of experimental work in the degree of precision and accuracy in classical chemistry in recent times.

As early as 1807 **Sir Humphry Davy** whose *name* is gratefully remembered for the invention of the safety lamp, applied galvanic current in the isolation of alkali metals, thereby introducing a new technique in chemistry. The fruitful discoveries of the laws of electrolysis by Michael Faraday in 1832 and the law of conservation of energy by Robert Meyer in 1842, the enunciation of the Kinetic Theory of gases by Clausius, Maxwell and others, and the investigations on colloids by Graham, and on solutions by Raoult and **Arrhenius** (1859-1928) were undoubtedly contributions of unparalled importance in theoretical chemistry in the nineteenth century.

Orgainic chemistry also made steady and phenomenal progress since 1828—the year Wohler disproved the 'theory of vital force' by the synthesis of urea from purely inorganic materials. The development in Organic Chemistry was mainly due to the efforts of **Liebig, Kekule, Emil Fischer, Van't Hoff** and many others of scarcely less celebrity.

Towards the end of the nineteenth century the rare gases of the atmosphere were discovered by Lord Rayleigh, Sir William Ramsay and Travers.

The discovery of the phenomenon of radioactivity and the radioactive elements in 1898 mainly due to the genius and superhuman efforts of **Madame Curie** (1867-1934), created a world-wide interest in the present century—an epochal discovery that was destined to lead to a revolution in scientific thought in the twentieth century. Researches on radioactivity and X-rays, coupled with the earlier works on the conduction of electricity through gases, led to the structure of matter by **Sir J. J. Thomson, Lord Rutherford, Niels Bohr,** and many other distinguished scientists. The significance of atomic number and its bearing on the structure of atoms was first grasped by Moseley in the year 1913, and in the same year the isotopes of elements were discovered by Soddy. The electronic theory of valency, developed by Langmuir, Lewis and Kossel, largely explained the cause of many chemical changes in a very convincing manner. With the elucidation of the structure of atoms the Transmutation of elements—the dream of the alchemists—has become a reality mainly due to the pioneer works of the celebrated scientists Rutherford, **Chadwick, Lawrence, and Irene Curie,** daughter of the discoverers of radium, and many others equally famous. Other discoveries of outstanding importance within the last few years have been the nuclear units, neutron and positron, by Chadwick and Anderson respectively in the year 1932. Heavy water, and heavy hydrogen, also called deuterium, were discovered by Urey in the same year. But of all the discoveries the fission of uranium with the release of unbelievable amount of energy is undoubtedly the most unique in the present century. The discovery of transuranic elements by **Seaborg** *et al* in recent years has greatly widened the boundaries of inorganic chemistry.

Exercises

1. What is chemistry ? Discuss its scope, and impact on civilisation.
2. Trace the development of science of chemistry.
3. Write an essay on : "whether the science of cheristry is a blessing or a curse for humanity depends on the use to which it is put." *Punjab Inter.,* '31.

II

FUNDAMENTAL CONCEPTS

Matter.—Our active existence consists largely of our relations with an infinite variety of things around us. As we look about, we come across many objects which form the external world around us, differing from each other in size, shape, colour, and such other properties as can be *perceived by one or more of our senses*—touch, sight, hearing, smell and taste. Any one object does not usually affect all our senses, but we see and feel most things. Substances that are invisible may be felt or smelt ; the poisonous sewer gas, for example, may be perceived through the sense of smell ; we feel the presence of air when the wind blows. In general we become aware of the existence of a substance by the sense impressions it produces in our minds. Each kind of substance, therefore, that comes to our *senses* in our everyday experience, be it common or rare, useful or useless, is included in the general term matter. The different kinds of matter that compose the universe are termed *materials*. Each material body has its own distinguishing characteristics, otherwise called its *properties*, by which it can be recognised or identified and separated from other materials. Sugar is one material, iron is another, glass another. One may identify a white substance as sugar, if it is sweet. Sweetness is one of the properties of sugar. Iron has the property of rusting in moist air ; glass the properties of brittleness and transparency. These differences in essential properties are due to the fact that *substances may differ in composition*. Difference in composition of various kinds of matter gives rise to difference in properties. Sugar and salt are two materials of different composition and hence they differ in many of their properties. These differences exist, quite apart from any particular size or shape of the materials. A lump of sugar and powdered sugar are but two different forms of the same material. To alter its sweetness, it must be transformed into something else which is not sugar, i.e., into a different substance.

A substance retains its specific properties so long as its composition remains the same. Various material substances may differ in their essential properties, but all of them occupy some *space* and possess some *weight*, and what is called *inertia* by virtue of which a substance requires a *force* to set it in motion, and if already in motion, to alter the motion. Air, earth, water, rock, wood, glass and iron are a few familiar forms of matter.

Matter possesses mass (which we measure by weight) and inertia, occupies space and may be perceived through one or more of our senses.

Three States of Matter.—Matter may exist in three states, *viz.*, *gas, liquid and solid.* Matter in the gaseous state possesses the property of filling completely and uniformly any available space. A gas is characterised by its lack of definite shape or volume. It assumes the shape of the containing vessel which it fills completely and to a uniform density. Hydrogen, oxygen, nitrogen, and carbon dioxide are examples of gaseous substances. Matter in the liquid state possesses no shape of its own ; it takes the shape of the vessel in which it is contained, but it does always retain a definite volume. Oil, water, alcohol, milk, mercury and petrol are liquid substances. Solids are distinguished by having sufficient rigidity to maintain a definite shape. A substance in the solid state has got a definite shape and size of its own. A piece of wood will always have the same shape and will always occupy the same space.

It must be observed that the same substance may exist in any one of three states of matter ; ice, water, and steam, for example, are all the same thing so far as the kind of matter is concerned but their physical states are different. With ordinary conditions of temperature and pressure a substance exists in one state only, solid, or liquid, or gas. But a substance may pass from one physical state to another by controlling such factors, as temperature and pressure. All gases can be liquified and all liquids solidified under a high pressure and a low temperature. Carbon dioxide is normally gaseous, but at a low temperature and a comparatively high pressure it becomes a liquid, and at a still lower temperature it becomes a solid, popularly known as **dry ice.** When a solid is heated, its temperature gradually rises until at a given temperature the solid is converted into a liquid—this temperature which is characteristic for a given solid, is known as the **melting point** or the **fusion point** of the solid. Such a process of converting a SOLID INTO A LIQUID by heat is called FUSION and the reverse process of converting a liquid into a solid by cooling is known as FREEZING. The **freezing point** of a pure liquid is the same as the melting point of the solid obtained from it by cooling. Ice melts at 0°C and tin at 232°C. It does not, however, follow that any and every solid can be transformed into a liquid by heat ; wood, for example, does not liquefy but burns on heating.

When a liquid is heated, its temperature gradually rises up to a definite point called the **boiling point** of the liquid, when along with the formation of bubbles inside it, the liquid begins to vaporise briskly. There is a rapid vaporisation throughout the mass of the liquid during boiling. **Vaporisation** is, thus, the process of converting a liquid into the vapour state, and the reverse process of converting the vapours into the liquid state by cold is known as **condensation.** A pure liquid has a characteristic boiling point ; pure water boils at 100°C under a pressure of one atmosphere ; mercury boils at 356.95°C.

$$\text{Solid} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{liquid} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{gas}$$

Physical and Chemical changes.—Constant changes seem to be inevitable law of nature. Matter undergoes two kinds of changes. Many changes take place which do not affect the composition of a substance ; these are referred to as physical changes. A change that affects the composition of a substance is known as a chemical change.

Illustrations : (i) A lump of sugar, if broken to pieces, still remains sugar ; the powdery sugar tastes as sweet. But when strongly heated, it loses its colour and sweetness and chars into a black mass which is not sugar, i.e., the composition of sugar has been altered. Sugar is said to undergo a physical change in the first instance and a chemical change in the second case. When sugar dissolves in water, it undergoes a physical change, since it is not chemically changed in being dissolved. It retains its sweetness even in solution. The whole amount of sugar may be recovered, unchanged in mass and composition, on evaporating the solution to dryness.

(ii) On dropping a few crystals of iodine in a heated flask, the latter is filled with violet vapours of iodine ; this is a physical change.

(iii) When a piece of iron *rusts* in moist air, it becomes a *reddish brown* powder. During rusting iron has combined with the oxygen of air, forming a new substance, called iron oxide, which is the rust. Iron+oxygen = iron oxide (rust). This is a chemical change.

(iv) When a piece of steel is magnetised, its colour, density, tenacity, mass and the composition and hence the chemical properties remain unaltered. This is a definite physical change. The change is easily reversed on heating.

(v) A piece of platinum becomes white-hot on heating and emits light. It is, however, restored to the original state on cooling. This is another example of a physical change.

(vi) When water is heated until it vaporises, it becomes steam. But the steam becomes water again on cooling, and hence it is the same substance as water. The vaporisation of water is a physical change. Again cooling freezes water into ice ; ice melts into water when heat is applied. Ice, water and steam are but different forms of the same substance, and all of them have the same composition, and hence the same chemical properties. The transformations of water into ice and steam are undoubtedly physical changes.

(vii) When a piece of magnesium is burnt in air, it gives a blinding white light—the ash that is left is different from the magnesium in its properties. Like magnesium, it does neither burn nor does it liberate hydrogen from dilute sulphuric acid. The ash weighs more than the magnesium that was burnt, since during combustion the latter has combined with the oxygen of air producing the ash which is magnesium oxide and is white in appearance. This change takes place with evolution of heat. This is a chemical change.

Magnesium+oxygen = magnesium oxide.

The white magnesium oxide when strongly heated in air, glows with a bright light. On cooling there is no change in the substance. The glowing is a physical change.

(viii) When a piece of clean copper wire (rose-red in colour) is heated in a Bunsen flame, it colours the flame green. The heating is continued until it no longer gives any green colouration. It has now turned black due to its conversion into a new substance, called copper oxide. This is a chemical change.

Copper + oxygen = copper oxide (black).

(ix) When water is sprayed on to a lump of quick lime, the latter crumbles to powder with a hissing noise and evolving much heat. Quick lime has become slaked lime by combining with water. This is a chemical change.

Quick lime + water = slaked lime.

(x) **Electrolysis of water.**—When an electric current is passed through water, acidified with dilute sulphuric acid, it is decomposed into two new substances hydrogen and oxygen. This is obviously a chemical change. Since water is a bad conductor of electricity, it is acidified with dilute sulphuric acid before electrolysis. The electrolysis is carried out in an apparatus, called a voltameter (fig. 3); it consists of three glass tubes—the central one carrying a funnel acts as a reservoir of water, and the two graduated tubes at the bottom of which are fused two platinum foils are the collecting vessels. The voltameter is filled with the acidulated water through the funnel, and the two platinum foils are connected to the negative and positive poles of a battery. On passing the electric current, bubbles of gas rise from each electrode and collect into the two side tubes—the volume of the gas at the negative electrode, called the **cathode,** is twice that of the gas at the positive electrode, known as the **anode.** The gas liberated at the cathode, burns with a pale blue flame, and is known as hydrogen ; the gas that is liberated at the anode, rekindles a glowing chip of wood, and is called oxygen. Thus, *water is decomposed by electrolysis into two volumes of hydrogen and one volume of oxygen.*

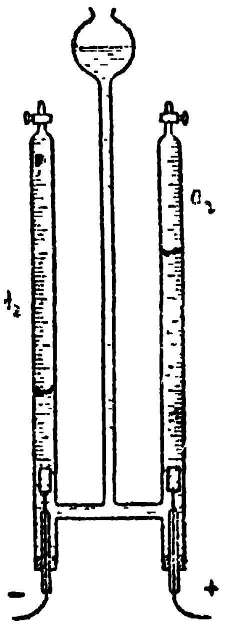


FIG. 3

(xi) *Decomposition of mercuric oxide.*—When red oxide of mercury, also called mercuric oxide, is heated in a test tube, the colour changes to black, but on cooling the red colour of the substance is restored. No change has occurred in the mercuric oxide itself ; this is a physical change. But when strongly heated the mercuric oxide breaks up into two new substances mercury and oxygen :

Mercuric oxide = mercury + oxygen

A shining mirror of mercury is deposited on the upper part of the tube. A glowing splint held at the mouth of the tube, is rekindled showing that a gas, called oxygen, is given off. This is a chemical change.

(xii) When some potassium chlorate is heated in a test tube, it melts and effervesces, and decomposes into oxygen and potassium chloride. The oxygen is given off, and the potassium chloride is left as a residue. This is a chemical change.

Potassium chlorate = potassium chloride + oxygen

(xiii) A few crystals of iodine are sprinkled on small pieces of white phosphorus taken on a sand-tray ; the phosphorus readily takes fire, and a chemical change occurs.

(xiv) When pellets of mercuric thiocyanate are ignited by the flame of a taper, they burn, swelling into a curious worm-like structure, the so-called **Pharaoh's Serpent.** This is a chemical change.

Characteristics of physical and chemical changes.—Some of the main characteristics of physical and chemical changes are :

(i) A physical change alters only the physical properties of matter. Physical properties of matter include the familiar properties directly perceptible to our senses, such as colour, odour, taste, size, shape, etc. which may be observed without transformation into new substances. *No new substance is produced in a physical change.*

A chemical change alters the specific chemical properties of a substance. The chemical properties of a substance are related to its capacity for being transformed into substances of other kinds. *New substances with different properties are produced in chemical changes.*

(ii) A physical change is usally *temporary*, and can easily be reversed by appropriately altering the external conditions such as pressure and temperature; the chemical change, on the other hand, is permanent and cannot be easily reversed.

(iii) The weight of a substance remains unaltered in a physical change; the weight of a material usually alters when it is transformed into a new substance.

(iv) A physical change is not usually accompanied by marked evolution or absorption of heat, except when the latent heat is absorbed in the change of state such as melting and evaporation ; a chemical change, on the other hand is always attended with either evolution or absorption of heat.

The indestructibility of matter.—In 1774 the great French savant Lavoisier put forward the law of conservation of mass which forms the basis of all quantitative works in chemistry. Matter can undergo changes or what are called transformations from one form into another. But the law states that :

The mass of a system remains unaltered by any change that takes place within it. In other words, *matter can neither be created nor destroyed. There is* therefore, *no change in the total mass of matter when a chemical change occurs*, i.e., the total mass of matter before the change is equal to the total mass of matter after the change. Hence, within limits of experimental error, the sum of the weights of the products must be equal to that of the weights of the reactants in a chemical reaction. In other words there can be no gain or loss of matter accompanying a chemical change. Thus, when a certain weight of mercuric oxide, say 15 grams, is completely decomposed by strong heat into mercury and oxygen, the total weight of mercury and oxygen must also be 15 grams.

$$\text{Mercuric oxide} = \text{mercury} + \text{oxygen}$$

$$\therefore \text{ wt. of mercuric oxide} = \text{wt. of mercury} + \text{wt. of oxygen.}$$

The above principle is usually referred to as *the law of conservation of mass*, or *the law of indestructibility of matter*, since the weight is proportional to mass, which measures the quantity of matter.

Illustrations : (i) Lavoisier's experiment.—Lavoisier was the first to explain and establish the law of conservation of mass. In one of his experiments he heated a piece of tin in a SEALED retort containing air, when a part of tin was calcined into its oxide. The apparatus was weighed before heating and was allowed to cool after heating and weighed again. *No change in weight* was found proving that there was no loss or gain of matter during the calcination of tin which was a chemical change.

(ii) **Charcoal Experiment.**—When a piece of charcoal is ignited, it continues burning and finally disappears completely. This simple experiment suggests an *apparent* loss of matter. But this is actually not the case. The piece of charcoal unites with the atmospheric oxygen during burning, forming carbon-dioxide gas which passes into the atmosphere, and hence the apparent loss of matter. But if the weight of oxygen used up is taken into consideration, there would occur no loss or gain in weight as the charcoal burns—the sum of the weights of charcoal and oxygen would be found to be equal to the weight of carbon dioxide formed.

The following experiment on *combustion of charcoal* clearly demonstrates it. A piece of charcoal is burnt in oxygen in a closed space so that no material can escape. A round-bottom flask (fig. 4) is provided with a tightly fitting rubber-stopper, through which pass two copper wires. One of the wires carries a spoon on which a piece of charcoal rests. A platinum wire, touching the charcoal, joins the two copper wires. The flask is filled with oxygen—the tubes A and B are meant for filling the flask with oxygen, and then carefully weighed in a balance. The two copper wires are then connected to the two terminals of a battery, and an electric current is passed through the platinum wire which becomes red hot and ignites the charcoal. The current is passed until the charcoal disappears completely with the formation of carbon dioxide :

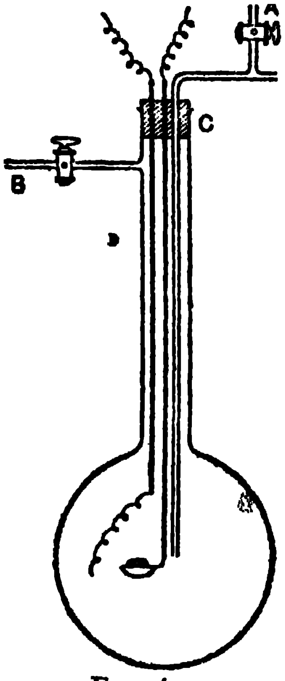


FIG. 4

Charcoal + oxygen = carbon dioxide

The battery is then disconnected, and the flask is cooled and weighed again. The weight is found to be the same as before. Hence matter is neither created nor destroyed during the transformation of charcoal into carbon dioxide.

(iii) **Candle Experiment.**—When a candle burns in air, it gradually disappears, leaving hardly anything. There is thus an *apparent* loss of matter. But actually the material of the candle which is wax, is not lost on combustion. It is changed into two gaseous substances, carbon dioxide and water vapour, which escape into the atmosphere, and hence the apparent loss in weight. But it may be shown by the candle experiment that the products of the change, the carbon dioxide and water vapour, weigh more than original candle itself, since a part of air, which is oxygen, is used up when the candle burns. If however, a proper balance sheet is drawn up, it would be seen that the weights of materials used up on one side and those formed on the other do exactly blance :

Candle + oxygen = carbon dioxide + water vapour.

In the candle experiment a small candle is placed on a perforated cork (to admit air) at the bottom of a glass chimney, the top of which is connected with a U-tube containing pieces of caustic potash in one limb and fused calcium chloride in the other. The chimney with the U-tube is carefully weighed in a balance. Then the U-tube is connected on the other side with an aspirator full of water (fig. 5). The candle is now lighted and quickly replaced, and the water is allowed to run out of the aspirator when air enters the chimney through the perforations in the cork. The candle continues to burn in the draught of air caused by the suction in the aspirator. After a few minutes the tap of the aspirator is turned off and the candle goes out. The chimney with the U-tube is then cooled and weighed again. It is found that far from a *loss* of weight occurring when the candle burns there is actually an increase in weight. This increase in weight is not, however, due to any creation of matter but due to the fact that the matter which is the candle, instead of being destroyed during burning, has united with the oxygen of air to form carbon

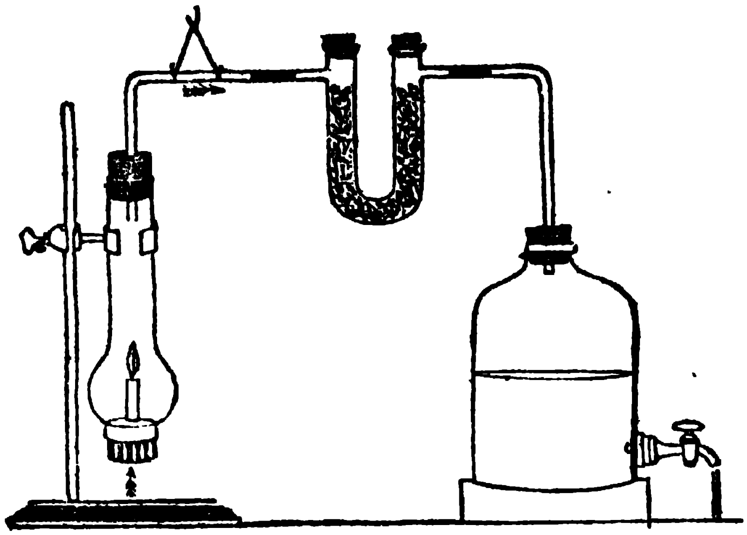


FIG. 5

dioxide and water vapour which have been absorbed by the caustic potash and the calcium chloride respectively and hence the increase in weight.

(iv) When a piece of iron rusts in moist air, it increases in weight. There is an *apparent* creation of matter in this instance. But the gain in weight is due to the fact that a part of air which is oxygen, is used up in the rusting of iron. The total weight of the iron and the oxygen consumed is, however, equal to that of the rust formed.

Iron + oxygen = rust.

(v) Similarly, when a piece of magnesium ribbon is heated in air, it burns away to a white powder, called magnesium oxide, which weighs more than the original magnesium. It appears to violate the law of conservation of mass. The gain in weight of magnesium when it burns is equal to the oxygen of air used up. Hence the total weight of magnesium plus oxygen used up is equal to the weight of magnesium oxide produced: Magnesium + oxygen = magnesium oxide.

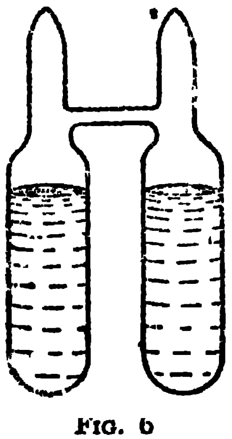


FIG. 6

(vi) **Landolt's Experiment.**—The law has been tested over and over again and hence the general validity of the law. The law was put to the most rigid test by Landolt between the years 1899 and 1906. In one of his experiments, the reacting material, e.g., *ferrous sulphate* and *silver sulphate* solutions, in the two arms of an H-tube (fig. 6), was sealed off. It was then weighed very accurately. Then the solutions were mixed together by tilting the tube, when the reaction took place—the silver sulphate was reduced to metallic silver by the ferrous sulphate. The reaction over, the tube was allowed to cool for some time and weighed again. It was found to weigh the same as before. Hence the truth of the law.

Similar experiments can easily be carried out in the laboratory. In one experiment, some ferric chloride solution in a test tube is placed in a conical flask containing potassium ferrocyanide solution. The flask is then corked and weighed, The two solutions are mixed together by tilting the flask, when a deep blue precipitate forms. There is, however, no change in weight. The experiment may be repeated with solutions of mercuric chloride and potassium iodide ; on mixing the two solutions a yellow precipitate (which rapidly turns red) of mercuric iodide is produced—the precipitate, however, dissolves in an excess of potassium iodide solution.

In the strictest sense the law of conservation of mass is also admitted to be inexact, in as much as many chemical changes are actually accompanied by a slight loss or gain of weight, the reasons being that *mass and energy are interconvertible*—the equivalence of mass and energy being expressed by the equation :

$$E = mc^2 \qquad \therefore \quad m = E/c^2.$$

where E = the energy and m = its mass equivalent in grams ; c = the velocity of light = 3×10^{10} cm. per sec.

$$\therefore \quad E = m \times (3 \times 10^{10})^2 = 9 \times 10^{20} \text{ m ergs.}$$
$$= 9 \times 10^{20} \text{ m}/4.184 \times 10^7 = 2.15 \times 10^{13}\text{m calories}$$
$$(1 \text{ calorie} = 4.184 \times 10^7 \text{ ergs.})$$

Therefore a chemical change attended by a loss or gain of energy E, usually as heat, would give rise to a corresponding loss or gain of weight $m = E/c^2$. But since c is very large, the change of mass due to liberation of energy is insignificantly small and consequently negligible in ordinary reactions. The combustion of 1 gram atom, i.e., 12 grams, of carbon, for example, is accompanied by an evolution of 97000 calories of heat, the corresponding loss of weight follows from the relation : $97000 = 2.15 \times 10^{13}$m, $\therefore$ $m = 4.5 \times 10^{-9}$ gm. i.e., to produce a loss of 1 mgm. it requires the combustion of about 2.7 tons of carbon—an infinitesimally small descrease in weight undetectable by any known means. The law of conservation of mass, in its simple form, therefore, holds good for ordinary chemical reactions.

The Law of Conservation of Energy.—Very much like matter, energy may be transformed from one kind to another without any gain or loss in the total amount of energy in the universe, i.e., the total amount of energy in the universe remains constant ; it *can neither be created nor destroyed* : but unlike matter, it possesses no weight nor does it occupy any space. The energy of a body may be defined as its power to perform work. Heat, light, electricity, motion, etc., are the familiar forms of energy. Whenever one form of energy disappears, an equivalent amount of energy of other kind or kinds must appear. Heat under the boiler generates steam which drives the engine. The engine produces motion which is utilised in running a dynamo. The dynamo generates electric current which may turn a motor.

Matter cannot undergo any change by itself ; the change is brought about by energy. Natural phenomena are nothing but manifestations of interplay between matter and energy.

Exothermic and endothermic changes.—The chemical changes which matter undergoes are almost always attended with more or less marked changes in energy, which usually manifests itself with the evolution or absorption of heat. The chemical changes which take place with evolution of heat are known as **exothermic changes,** while those taking place with absorption of heat are referred to as **endothermic changes.**

Coal is the transformation product from the vegetable matter of the remote past, and contains the stored-up energy of the sunlight which the plants absorb as they grow. Coal is the store-house of solar energy. This energy is released and appears as heat when the coal burns in air. In like manner, when carbon burns in oxygen, forming carbon dioxide, the process is accompanied by evolution of much heat ; this is an exothermic reaction. The heat evolved is due to the release of energy contained in the reacting materials. Hence carbon dioxide contains less energy than the constituent elements. Compounds, such as carbon dioxide, water, hydrochloric acid, etc., which are formed from their elements with evolution of heat are known as **exothermic compounds.**

When sulphur vapour passes over red-hot charcoal, a colourless liquid, called carbon disulphide, is formed. Its formation takes place with absorption of heat which is contained in it. Hence carbon disulphide contains more energy than its constituent elements. Compounds, such as carbon disulphide, nitric oxide, and hydriodic acid, etc., which are formed from their elements with absorption of heat are known as **endothermic compounds.**

Endothermic compounds are very reactive, very easily decomposed, and are only formed from their elements at high temperatures. Exothermic compounds, on the other hand, are formed from their elements at low or moderate temperatures. They are less reactive and less easily decomposed than endothermic-compounds.

Varieties of matter.—Although there are a vast number of different chemical substances, it is now realised that there are only ninety-two distinct species from which these numerous substances are composed. The simple species or types of matter are called *elements*. Various forms of matter are classified into elements and compounds according to their composition.

The era of modern chemistry begins with Robert Boyle who in the seventeenth century overthrew the theory of four elements of Aristotle by clearly distinguishing elements as '*substances which cannot be decomposed further.*'

Element.—*An element may be defined as a substance which cannot be decomposed into any simpler substances by means of ordinary chemical reactions.*

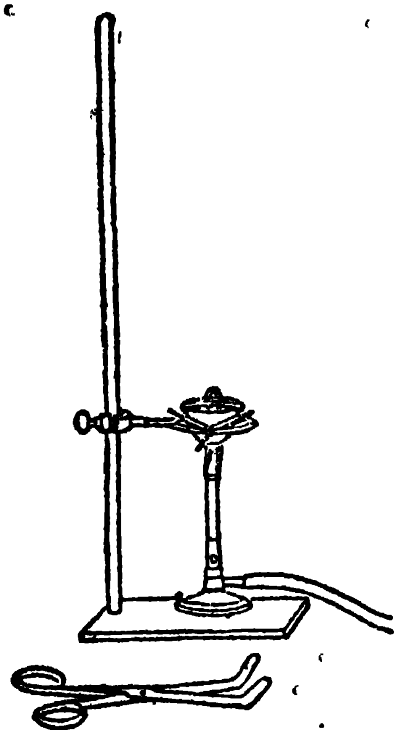


FIG. 7

Magnesium is an element. It cannot be decomposed into anything simpler than magnesium. A piece of magnesium ribbon, weighing about 0.5 grams, is slowly heated in a loosely covered porcelain crucible (fig. 7) till combustion is complete. The crucible is then heated strongly for some time, cooled, and weighed. There is an increase in weight. The magnesium has combined with oxygen from the air to form magnesium oxide, which is a white powder :

Magnesium + oxygen = magnesium oxide.

If the magnesium were decomposed into simpler substances, the white powder and something else, the white powder must weigh less than the magnesium. But the white powder weighs more, and hence the magnesium has become something more complex by taking oxygen from the air. We can, therefore, add to an element, but we cannot decompose it.

Copper, silver, gold, iron, tin, lead, magnesium, aluminium, carbon, sulphur, hydrogen, oxygen, nitrogen, etc., are few familiar elements.

There are ninety-two (taking the elements beyond uranium, namely, neptunium, plutonium, americium, curium, berkelium, californium, einsteinium, fermium mendelevium and nobelium into account, the number is one hundred and two) elements but not a few of them are very rare—some are no more than laboratory curiosities. The distribution of elements in the earth's crust is shown in the following diagram (fig. 8). The elements vary greatly in relative abundance. Oxygen, silicon, aluminium, iron, calcium, sodium, potassium, and magnesium are the eight most common elements which make up about 97 per cent of earth's crust, the ocean and the atmosphere.

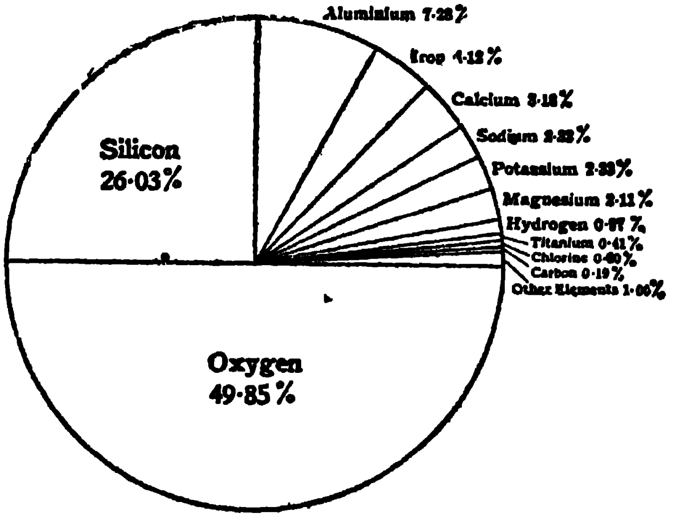


FIG. 8

Their relative abundance in percentages are as shown in fig. 8. Oxygen alone makes up about half of the weight of earth's crust, eight-ninths of the ocean, and about a fifth of the atmosphere.

Compound.—*A compound may be defined as a substance which is formed by the chemical union of two or more elements in a definite proportion by weight, and as such it may be separated into two or more elements.*

Compounds may either exist in nature or have been prepared in the laboratory. Mercuric oxide, also called red oxide of mercury, is a compound, as it breaks up into mercury and oxygen by strong heat.

About 2 grams of mercuric oxide are taken in a hard glass test tube (fig. 9) fitted with a rubber stopper through which passes a glass delivery tube leading to a pneumatic trough containing water, a gas jar full of water, is inverted in the trough,—the mouth of the jar being supported on a beehive shelf over the delivery tube. The test tube is clamped in a horizontal position. On heating the mercuric oxide, bubbles of gas collect in the jar, and at the same time a shining mirror of mercury deposits on the cooler part of the tube. The gas rekindles a glowing chip of wood, which burns with a brilliant flame, indicating that the gas is oxygen :

Mercuric oxide = mercury + oxygen.

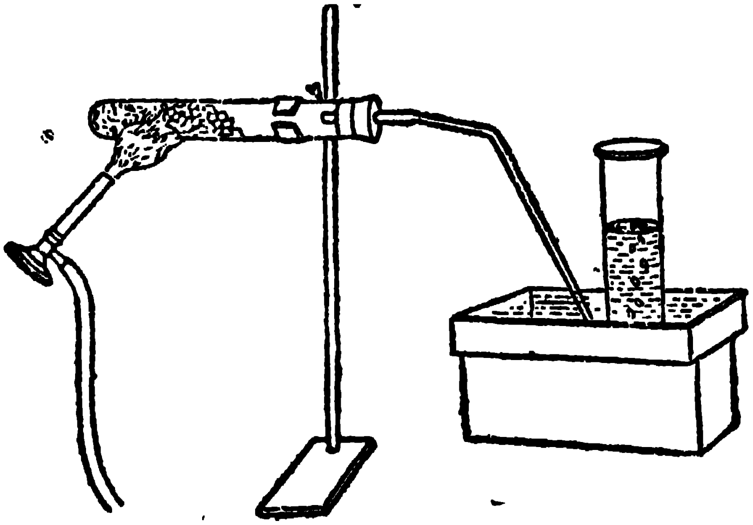


Fig. 9

When an electric current is passed through water acidified with dilute sulphuric acid, it decomposes into hydrogen and oxygen, indicating that water is a compound. Fused common salt may be decomposed into sodium and chlorine by passing electric current through it.

Mixture.—*A mixture, sometimes called a mechanical mixture, is obtained by the mere blending, without any chemical union whatsoever, of different substances (elements or compounds), which are easily identified in the mixture by their respective properties which remain unaltered.*

The gun-powder is a mixture of three materials, nitre, also called potassium nitrate, charcoal, and sulphur. Air is a mixture of nitrogen and oxygen mainly.

Mixtures and compounds.—A mixture differs from a compound in the following respects :

(i) *The components, or what are called the ingredients, of a mixture retain their specific properties ; a compound, on the other hand, possesses properties which are peculiar to itself alone and are entirely different from those of its components.*

A mixture of 7 grams of clean fine iron filings and 4 grams of flowers of sulphur is heated in a test tube, when the whole mass glows—the change takes place with evolution of much heat. When cold, the tube is broken in a mortar, and the resulting black mass is powdered. When the powder is examined under a lens, no particles of sulphur or iron are visible in it, although these can be seen in the mixture. When a magnet is brought before the new substance no iron is attracted, as it is from the mixture. Carbon disulphide, a liquid which dissolves sulphur, does not dissolve out any sulphur from the new substance. Hence iron and sulphur have disappeared as such, forming a new substance, called ferrous sulphide, which is a chemical compound.

When a mixture of iron filings and sulphur is treated with dilute sulphuric acid, a gas is given off which burns with a pop. The gas is hydrogen, and is formed by the action of the acid upon the iron filings. The sulphur is not attacked and is left over when all the iron has dissolved. When, however, the iron sulphide, also called ferrous sulphide, is acted upon with dilute sulphuric acid, a gas is evolved which smells of rotten eggs. The gas is hydrogen sulphide ; it burns but not with a pop.

These experiments show that the new substance is entirely different from its constituents in properties.

(ii) *The components of a mixture are easily separable by physical means ; a compound may, however, be separated into its constituents by chemical means, but not by any physical method.*

If a mixture of iron and sulphur is shaken with carbon disulphide, and filtered and the filtrate is allowed to evaporate, yellow crystals of sulphur are deposited. A magnet can attract the iron filings from the mixture. Thus, sulphur and iron can be removed from the mixture by physical means. But it is only by chemical methods that iron and sulphur can be obtained from iron sulphide. Thus, to get sulphur from iron sulphide the substance is treated with dilute hydrochloric acid, and the foul-smelling gas that evolves is burnt, and if a cold crucible lid is held in the flame, sulphur is deposited.

(iii) *The composition of a mixture is variable but the composition of a compound is fixed and definite.* Fixed composition is one of the best tests for a compound.

In whatever way the iron sulphide is prepared it must always contain 7 parts of iron to 4 parts of sulphur. When more iron than what is required by this proportion is heated with sulphur, the excess iron remains over, mixed with iron sulphide, and can be removed from it with a magnet. When an excess of sulphur is used, it does not combine ; it burns away or remains mixed with iron sulphide from which it can be dissolved out with carbon disulphide.

(iv) *Heat is either evolved or absorbed during the formation of a compound from its elements ; but when a mixture is made there is usually no heat change.*

Much heat is evolved during the formation of iron sulphide, but not when iron filings and sulphur are merely blended together. Heat change sometimes accompanies the formation of a solution which is a mixture, e.g., much heat is absorbed when ammonium chloride is dissolved in water ; when water is added to sulphuric acid the solution becomes extremely hot.

(v) *A mixture is usually heterogeneous i.e., not perfectly uniform, whereas a compound must be always homogeneous, i.e., the same throughout.*

This criterion obviously does not hold for solutions which are perfectly homogeneous mixtures. A magnifying glass reveals distinct particles of iron filings and sulphur in their mixture, but not in iron sulphide.

(vi) *A compound, being a pure substance, has fixed melting and boiling points, whereas a mixture usually has no definite melting or boiling point.*

A Homogeneous Substance is one in which every part of the substance has exactly the same composition and properties as every other part. Crystals of copper sulphate, common salt, etc., are homogeneous bodies. A compound *must* be homogeneous, since it contains only one kind of substance.

A Heterogeneous Substance exhibits different properties in its different parts. Gun powder is a heterogeneous mixture of nitre, sulphur and charcoal. A heterogeneous substance must be a mixture.

Metals and non-metals.—The elements are divided into two main classes, viz., *metals and non-metals*, on the basis of their properties. The classification, though convenient, is somewhat arbitrary, since their properties sometimes overlap. Thus, there are elements which exhibit more or less the properties of both metals and non-metals, they are referred to as *metalloid.*

Potassium, sodium, calcium, magnesium, aluminium, zinc, iron, tin, lead, copper, mercury, silver, platinum, and gold are some of the familiar metals. Hydrogen oxygen, nitrogen, phosphorus, fluorine, chlorine, bromine, iodine, carbon, silicon, boron, and sulphur are examples of non-metals. Arsenic and antimony are metalloids.

The main features of difference between metals and non-metals are :

Physical differences

METALS	NON-METALS
1. Metals possess *lustre, described* as metallic lustre, and *reflect light* from polished or freshly cut surface.	Non-metals have *no lustre* (except graphite and iodine which are lustrous) and *do not reflect light.*
2. Metals usually *have high densities* with several exceptions ; lithium, for example, is a light metal with a density of 0.53 only ; sodium, potassium, calcium, magnesium and aluminium also have low densities. Metals with densities greater than 5 are called *heavy meatls*—osmium with a density of 21.3 to 24 is the heaviest.	Non-metals have *low densities,* all below 5—liquid hydrogen, density 0.076, is the lightest, and iodine with a density of 4.93 is the heaviest.
3. Metals are usually *good conductors of heat and electricity.* Silver is the best conductor ; copper is the next best. Mercury is not a very good conductor.	Non-metals are *poor conductors of heat and electricity* except graphite. Arsenic has also marked conductivity.
4. Metals possess *tenacity* and *toughnes,* i.e., possess resistance to rupture by a stretching force and twisting respectively. Metals also possess *malleability* and *ductility,* i.e., possess the property of being hammered into thin sheets and drawn into wires respectively. Some metals, e.g., bismuth and antimony, are brittle. Gold is the most malleable metal—gold leaf 1/280000 of an inch in thickness may be made by hammering.	Non-metals possess none of the properties of tenacity, toughness malleability and ductility—non-metals are brittle, if solid.

5.	Metals are *solids* with the exception of *mercury* which is a liquid at the ordinary temperature. Gallium (m.p. 29.75°) and caesium (m.p. 28.45°) are low melting solids.	Non-metals are usually *gases*, or *volatile solids* or *liquids ;* thus amongst the members of halogen family, fluorine and chlorine are gases, *bromine is a liquid*, and iodine a volatile solid. The non-metals carbon, boron and silicon are non-volatile solids.

Chemical differences

	METALS	NON-METALS
1.	Metals are *electropositive* elements (i.e., they carry positive charges during electrolysis) ; in other words, they form *cations*, e.g., $ZnCl_2 \leftrightharpoons Zn^{++} + 2Cl'$. Metals may sometimes form part of complex anions, e.g., $KAg(CN)_2 \leftrightharpoons K^+ + Ag(CN)_2'$.	Non-metals are *electro-negative* elements, i.e., they form *anions* (i.e., they carry negative charges during electrolysis), or hardly show any electro-chemical character, e.g., carbon. Hydrogen, though a non-metal, is generally electro-positive and forms a cation, e.g., $HCl \leftrightharpoons H^+ + Cl'$.
2.	*Metals generally dissolve in HCl or dilute* H_2SO_4, giving off hydrogen—metals which are less electro-positive than hydrogen are, however, exceptions.	Non-metals *do not dissolve* in HCl or dilute sulphuric acid.
3.	Metals usually form *basic oxides*, e.g., CuO, Fe_2O_3, CaO, but some oxides such as ZnO, and Al_2O_3 are amphoteric ; some metallic oxides of higher valency are, however, acidic, e.g., CrO_3 and Mn_2O_7.	Non-metals form *acidic oxides*, e.g., SO_2, CO_2, P_2O_5 ; some oxides such as N_2O, NO, CO, etc., are neutral. $P_2O_5 + 3H_2O = 2H_3PO_4$
4.	Metals form *halides* which are *stable in presence of water*, e.g. NaCl, $CaCl_2$, etc., but some are partially hydrolysed i.e., decomposed by water—the hydrolysis is *reversible*, e.g., $FeCl_3 + 3H_2O \leftrightharpoons Fe(OH)_3 + 3HCl$ Metallic halides are mostly non-volatile, and conduct electric current in solution in water. Stannic chloride, $SnCl_4$, is a volatile, liquid, and a non-electrolyte.	Non-metals form *halides* which are usually *unstable towards water*,—most of them are decomposed by water ; the decomposition is *irreversible :* $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$. $SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl$ Carbon tetrachloride, CCl_4, is stable towards water.
5.	Metals generally form *complex salts* in which the metal may be in the *cation*, e.g., $[Cu(NH_3)_4]SO_4 \leftrightharpoons [Cu(NH_3)_4]^{++} + SO_4''$, or in the anion $K_4[Fe(CN)_6] \leftrightharpoons 4K^+ + [Fe(CN)_6]''''$	Non-metals *do not usually form complex salts ;* boron and silicon, however, may form complex fluorides, e.g., KBF_4 and K_2SiF_6.

The constitution of matter.—Mass of a body is the matter contained in it, but what constitutes a mass of matter ? Several Greek philosophers, over 2,000 years ago, suggested that all kinds of materials in the universe, however continuous they may appear to be, are composed of very minute particles, called **molecules**, which are much too small to be perceived individually.

Molecule.—*A molecule may be defined as the smallest particle of an element or a compound which can exit in the free state. A molecule possesses the chemical properties of a given type of matter.*

According to the atomic theory put forward by Dalton in 1803, an element is assumed to consist of extremely minute particles called **atoms.** The atom of each element has a characteristic weight.

Atom.—*An atom may be defined as the smallest particle of an element which can take part in a chemical change.*

Molecules are composed of atoms. The smallest unit of a compound is a molecule ; this can exist as such in the free state. With an element it is necessary to distinguish between atoms and molecules, because the atom may not be always capable of any prolonged existence in free state. In the case of inert gases of the atmosphere, viz., helium, neon, argon, krypton and xenon, and vapours of most metals, mercury for example, the atom is quite stable and capable of free and independent existence. For these elements, therefore, the atom and the molecule are identical. Usually, however, two or more atoms compose a molecule of an element. The molecules of the common gases hydrogen, oxygen, nitrogen and chlorine contain two atoms, and the molecules of phosphorus and arsenic contain four atoms.

A molecule of an element contains like atoms only. A molecule of a compound is composed of one or more atoms of each of two or more different elements. An element, therefore, is a substance that consists of atoms of one kind only ; a compound is a substance that consists of atoms of two or more different kinds. Since a compound has a definite composition, a molecule of compound must contain a fixed number of atoms.

For example, a molecule of water consists of 2 atoms of hydrogen and 1 atom of oxygen ; a molecule of sulphuric acid contains 2 atoms of hydrogen, 1 atom of sulphur, and 4 atoms of oxygen ; a molecule of potassium chlorate is made up of 1 atom of potassium, 1 atom of chlorine, and 3 atoms of oxygen.

Atoms remain unaltered in all ordinary chemical transformations. During a chemical change molecules of reacting substances first separate into atoms which then combine to form new molecules of the product. Hence :

A chemical change *is one in which the atoms of the reacting molecules are regrouped to form new molecules ; a* **physical change** *does not affect a molecule, and hence no new molecules are produced in a physical change.*

Atomic weight.—Every kind of atom, according to Dalton's atomic theory, has a definite and constant weight. The atoms of any one element all have the same weight, but the atoms of different elements have different weights.

As the atoms are extremely minute, their mass is exceedingly small being of the order 10^{-24} grams ; the mass of an atom of the lightest element hydrogen is only 1.67×10^{-24} grams ; the mass of an atom of uranium is 3.95×10^{-22} grams only. The smallness of an atom is rather difficult to grasp easily—about 3×10^{19} atoms of hydrogen are contained in 1 c.c. of the gas.

It is, therefore, difficult to find out the actual weight of an atom of an element. But the weight of the atom of the element *relative* to that of a standard atom can be easily found out—this relative weight is stated as the atomic weight of the element.

At one time the weight of the hydrogen atom, the lightest known atom was chosen as the standard by Dalton and its atomic weight was taken as unity. The atomic weight of an element relative to that of hydrogen as unity, therefore, showed how many times an atom of the element was heavier than the hydrogen atom.

The atomic weight is now-a-days determined in terms of the element oxygen as the standard—the atomic weight of oxygen is arbitrarily taken as 16.0000.

The atomic weight of an element is the weight of an atom of the element relative to the weight of the oxygen atom taken as 16.

The atomic weight of an element is, therefore, the number of times one atom of it is heavier than the sixteenth part of the atom of oxygen. On the oxygen standard the atomic weight of hydrogen is 1.008.

Exercises

Do you consider the following to be physical or chemical changes :
(a) common salt is shaken with water until no further solid remains,
(b) a magnesium ribbon is heated in air until it takes fire, ch
(c) a piece of sodium floats on water, finally disappearing, ch
(d) the dissolution of sugar in a cup of tea, phy
(e) ammonium chloride, when heated in a test tube, vaporises and condenses as a solid on the cooler part of the tube ? Give reasons. ph

2. What are the differences between physical and chemical changes ?

In what ways does a mixture of iron filings and sulphur differ from iron sulphide ?

3. A piece of iron rusts on exposure to the air and increases in weight, while a piece of charcoal when ignited, burns away leaving a little ash of negligible weight. How would you reconcile the above facts with the law of conservation of mass ?

Describe a suitable experiment to prove conclusively that matter is indestructible.

4. Define (a) element, (b) compound. State if each of the following is an element, a compound, or a mixture : common salt, water, mercuric oxide, sugar, gold, brass, a silver coin, potassium chlorate, air.

What are the chief differences between compounds and mixtures ?

5. What do you understand by the *atom, atomicity, atomic weight,* and *molecule* ?

The atomic weight of chlorine is 35.5. What does this statement convey to you ?

6. Classify the following changes as purely chemical, purely physical, or as belonging to both : (a) burning of kerosene oil, (b) distillation of water, (c) melting of lead, (d) magnetising a knife blade, (e) heating a piece of limestone, (f) souring of milk, (g) sending electric current through fused common salt, (h) dissolution of copper in nitric acid.

7. What is meant by exothermic and endothermic reactions ? Give two examples of each.

When some camphor is left in the air it completely disappears. Does this contradict the law of conservation of mass ?

III

Symbols, Formulæ & Equations

Symbols and formulæ.—In order to describe the chemical composition of a substance involving certain ones of the elements a chemist prefers to use, for the sake of convenience, abbreviations for the full name of each element concerned, since they are more quickly written. Thus, the letter H is written for the word hydrogen ; the abbreviation for oxygen is O ; and for nitrogen N. These are referred to as **symbols** of elements. Usually the symbol is the initial letter of the English name for which it stands ; when, however, more than one element has the same initial letter, a pair of letters are necessary ; thus, C stands for carbon ; Cl represents chlorine, and Ca is calcium. Ni is the symbol for nickel, and He for helium. Sometimes the symbols are derived from the Latin name of the element. The present system of chemical notation was introduced by the Swedish chemist Berzelius in 1811.

Symbols of a few elements with their Latin names in *italics* are given below :

Antimony (*Stibium*)	Sb	Mercury (*Hydrargyrum*)	Hg
Copper (*Cuprum*)	Cu	Potassium (*Kalium*)	K
Gold (*Aurum*)	Au	Silver (*Argentum*)	Ag
Iron (*Ferrum*)	Fe	Sodium (*Natrium*)	Na
Lead (*Plumbum*)	Pb	Tin (*Stannum*)	Sn

The symbol W for tungsten is derived from the German name wolfram.

Symbols of a few familiar elements are as follows .

Aluminium	Al	Iodine	I
Barium	Ba	Magnesium	Mg
Boron	B	Manganese	Mn
Bromine	Br	Nitrogen	N
Calcium	Ca	Oxygen	O
Carbon	C	Phosphorus	P
Chlorine	Cl	Platinum	Pt
Chromium	Cr	Silicon	Si
Fluorine	F	Sulphur	S
Hydrogen	H	Zinc	Zn

See the table of *International Atomic Weights*.

The symbol of an element does not only stand for the name but also represents *one atom or one atomic weight* of the element. Thus O does not stand merely for oxygen ; it represents one atom of oxygen, and also 16 parts by weight of oxygen. The letter N stands for nitrogen. It also means one atom of nitrogen and 14 parts by weight of nitrogen, and so on.

Formulæ.—Every substance, be it an element or a compound, has a definite chemical formula—a combination of symbols and numerals written in such a way as to indicate *what kinds of atoms* and *how many of each* are present in *each molecule* of the subtance. *A chemical formula symbolically represents the composition of a substance.*

The chemical formula of an element is denoted by its symbol with a numeral placed to its *right* and a little *below* it to show how many of its atoms are contained in a molecule. *The number of atoms contained in the molecule of an element is known as its* **atomicity.** Molecules of common gases oxygen, hydrogen, nitrogen and chlorine, each contain two atoms, i.e., their molecules are *diatomic* and consequently their formulæ are written as O_2, H_2, N_2 and Cl_2. A molecule of phosphorus contains 4 atoms, and hence its formula is P_4 But the inert gases argon, helium, and neon, etc., and most metallic vapours such as mercury and zinc, etc., are *monoatomic*, i.e., their molecules are composed of one atom only, and therefore, their formulæ are A, He, Ne, Hg and Zn, etc.

A molecule of a compound contains a fixed number of atoms of its constituent elements. Its chemical formula is designed by writing down side by side the symbols of its constituent elements, with a numeral to the right and slightly below each symbol in order to show how many atoms of it are contained in the molecule. Thus, a molecule of sulphuric acid contains 2 atoms of hydrogen, 1 atom of sulphur and 4 atoms of oxygen, and hence its formula is written as H_2SO_4—the numeral 1 being always understood. The formula for chalk, also called calcium carbonate, is $CaCO_3$, since it contains 1 atom of calcium, 1 atom of carbon, and 3 atoms of oxygen. Nitre, also known as salt-petre, is denoted by the formula KNO_3. H_2O stands for the formula of water.

The chemical formula of a substance does not merely denote *its composition*, it also represents *one molecule* or *one molecular weight* of it. Thus, water is represented by the formula H_2O ; it means that each molecule of water is composed of 2 atoms of hydrogen and and one atom of oxygen, and that its molecular weight is $18(2\times1+1\times16=18)$ parts by weight.

The molecular weight of a substance is the sum of the weights of atoms present in a molecule ; thus, the molecular weight of sulphuric acid, H_2SO_4, which contains 2 atoms of hydrogen, 1 atom of sulphur, and 4 atoms of oxygen, is : $2\times1+1\times32+4\times16=98$.

The formula for oxygen is O_2, and consequently, its molecular weight is $32(2\times16=32)$ parts by weight.

The molecular weight of a substance expressed in grams is called the **gram molecule** or sometimes the **gram molecular weight** ; thus 1 gram molecule of sulphuric acid is 98 grams ; one gram molecule of water is 18 grams, and one gram molecule of chalk is 100 grams, and so on.

A number placed to the immediate left of a chemical formula indicates the number of molecules of the substance. $5H_2SO_4$, for example, denotes 5 molecules of sulphuric acid ; $6H_2O$ means 6 molecules of water.

Two atoms of nitrogen are contained in a molecule of nitrogen, and its formula is wirtten as N_2 ; 2N, however, means 2 atoms of nitrogen; $5N_2$ stands for 5 molecules of nitrogen which contain 10 atoms of nitrogen ; 10 atoms of nitrogen are expressed as 10N. $7O_2$ stands for 7 molecules of oxygen ; 7O means 7 atoms of oxygen.

Valency.—**Chemical affinity** between substances is a measure of their tendency to undergo a chemical change. Quite commonly dissimilar substances exhibit greater chemical affinity—substances of opposite chemical nature easily enter into a chemical reaction ; thus a metal generally reacts easily with a non-metal. Again, it is found that the relative affinity of an element is not the same for different elements. Thus, chlorine is said to possess a greater affinity for sodium than for copper, since it reacts more readily and vigorously with sodium than with copper.

Chemical compounds are formed by the union of atoms of different elements in simple numerical proportions. It is, however, found that the combining power of atoms of different elements is not the same. Thus, if one atom of oxygen is considered, it is impossible to make more than 2 atoms of hydrogen combine with it. This holds good for all other elements. There is, therefore, a certain number of atoms of hydrogen with which one atom of an element would combine (if it combines with hydrogen at all). Thus, in the following compounds one atom of the elements combines with 1, 2, 3 or 4 atoms of hydrogen :

Hydrochloric acid	HCl	Ammonia	NH_3
Water	H_2O	Methane	CH_4

In these instances one atom of each of the elements chlorine, oxygen, nitrogen, and carbon are capable of combining with 1, 2, 3, and 4 atoms of hydrogen respectively, and consequently their **combining capacities,** or what is called **valency,** are 1, 2, 3, and 4 respectively. It is found that in none of the compounds of hydrogen does an atom of hydrogen combine with more than one atom of any element—the only exception in which one atom of hydrogen unites with more than one atom of another element is hydrazoic acid, N_3H ; and consequently an atom of hydrogen has the **least** combining capacity. Hydrogen has therefore, been chosen as the standard of valency, and its valency is taken to be 1. The valency of other elements is referred to that of hydrogen.

Valency.—*The valency of an element denotes the combining capacity of its atoms and is measured by the number of hydrogen atoms with which one atom of the element in question would combine.*

The examples cited above, therefore, tell us that chlorine, oxygen, nitrogen, and carbon are *univalent*, *bivalent*, *trivalent*, and *quadrivalent* respectively.

When an element does not directly combine with hydrogen, its valency is determined with reference to other elements of known valency. Thus, aluminium does not combine with hydrogen, but it combines with chlorine, forming the compound aluminium chloride, $AlCl_3$. Hence aluminium is trivalent, since *one atom* of it combines with *three atoms of univalent chlorine.* Oxygen is bivalent, and consequently when it combines with one atom of another element, the latter is also bivalent ; e.g., magnesium is divalent in magnesium oxide. MgO. The following oxygen compounds are highly illustrative :

Sodium monoxide Na_2O,	Magnesium oxide MgO,
Aluminium oxide Al_2O_3,	Silicon dioxide SO_2,
Phosphorus pentoxide P_2O_5,	Sulphur trioxide SO_3,
Chlorine heptoxide Cl_2O_7,	Osmium tetroxide OsO_4.

The above examples show that sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, and osmium are univalent, bivalent, trivalent, quadrivalent, pentavalent, hexavalent, heptavalent and octavalent respectively. 8 is the highest valency known.

The inert gases argon, helium, neon, etc., form no compounds with any elements, and as such they exhibit no valency. They are elements of zero valency. There are, therefore, nine valencies including zero, in all, which are exhibited by various elements, e.g., 0, 1, 2, 3, 4, 5, 6, 7 and 8.

Valency of metals may be determined by allowing their *equi-gram atoms* to act on hydrochloric acid and collecting the hydrogen evolved in graduated tubes. 23 mg. of Na, 24 mg. of Mg and 27 mg. of Al, for example, yield 11.2, 22.4 and 33.6 c.c.'s of hydrogen at N.T.P. respectively. Therefore, 1 gram-atoms of the said metals, i.e., 23 g. of Na, 24 g. of Mg., and 27 g. of Al, would yield 11.2,22.4 and 33.6 litres of hydrogen at N.T.P. respectively. But 1 gram molecule of H_2 occupy 22.4 litres at N.T.P. Hence 11.2 litres correspond to 1 gram-atom of hydrogen. Thus, 1 gram-atom of Na, Mg, and Al displace 1, 2, and 3 gram-atoms of hydrogen respectively, and hence their valencies are 1, 2 and 3 respectively.

Variable valency.—The valency of many elements may vary in different compounds. An element may exhibit more than one valency either (i) in its compounds with the *same* element ; thus iron is bivalent in ferrous chloride, $FeCl_2$, and trivalent in ferric chloride, $FeCl_3$; phosphorus is trivalent in phosphorus trichloride, PCl_3, but pentavalent in phosphorus pentachloride, PCl_5 or (ii) in its compounds with *different* elements ; thus nitrogen is trivalent in ammonia, NH_3, but pentavalent in nitrogen pentoxide, N_2O_5 ; sulphur is divalent in hydrogen sulphide H_2S, and hexavalent in sulphur hexafluoride, SF_6.

The valencies of some common elements are given below :

Element	Symbol	Valency	Element	Symbol	Valency
Aluminium	Al	3,5	Iron	Fe	2,3
Antimony	Sb	3,5	Lead	Pb	2,4
Arsenic	As	3,5	Magnesium	Mg	2
Barium	Ba	2	Manganese	Mn	2,3,4,6,7
Boron	B	3	Mercury	Hg	1,2
Bromine	Br	1,3,5,7	Nitrogen	N	1,2,3,4,5
Calcium	Ca	2	Oxygen	O	2
Carbon	C	4	Phosphorus	P	3,5
Chlorine	Cl	1,3,5,7	Potassium	K	1
Chromium	Cr	2,3,6	Silicon	Si	4
Copper	Cu	1,2	Silver	Ag	1
Fluorine	F		Sodium	Na	1
Gold	Au	,3	Sulphur	S	2,4,6
Hydrogen	H		Tin	Sn	2,4
Iodine	I	,3,5,7	Zinc	Zn	2

Variable valency of few metals and nomenclature of their compounds with reference to chlorides are noted :

Metal	Valency	Chloride
Cuprous copper	1	Cuprous chloride, CuCl
Cupric copper	2	Cupric chloride, $CuCl_2$
Mercurous mercury	1	Mercurous chloride, Hg_2Cl_2

Metal	Valency	Chloride
Mercuric mercury	2	Mercuric chloride, $HgCl_2$
Ferrous iron	2	Ferrous chloride, $FeCl_2$
Ferric iron	3	Ferric chloride $FeCl_3$
Chromous chromium	2	Chromous chloride, $CrCl_2$
Chromic chromium	3	Chromic chloride, $CrCl_3$
Manganous manganese	2	Manganous chloride, $MnCl_2$
Manganic manganese	3	Manganic chloride, $MnCl_3$
Stannous tin	2	Stannous chloride, $SnCl_2$
Stannic tin	4	Stannic chloride, $SnCl_4$
Plumbous lead	2	Plumbous chloride, $PbCl_2$
Plumbic lead	4	~~Public~~ chloride, $PbCl_4$ ~~Pamblic~~ Plumbic

Radicals.—In many compounds a group of atoms of different elements behaves collectively *like a single atom* and takes part *as a whole* in chemical reactions ; such a group of atoms is called a radical (also called *compound radical*). Thus, ammonia reacts with hydrochloric acid producing ammonium chloride, NH_4Cl, where the group NH_4, plays the part of a univalent metal and is called an *ammonium radical.*

The formula for sulphuric acid is H_2SO_4—the sulphate group SO_4, is bivalent since it combines with 2 hydrogen atoms. Similarly, the carbonate group CO_3, is bivalent in the carbonic acid, H_2CO_3 ; the nitrate group NO_3, is univalent in the nitric acid, HNO_3 ; the phosphate group PO_4, is trivalent in phosphoric acid, H_3PO_4.

The hydroxyl group OH in bases is a radical ; it is univalent ; e.g., caustic soda, NaOH.

Some common radicals with their valencies are as follows :

Radical	Valency	Radical	Valency
Ammonium NH_4	1	Carbonate CO_3	2
Sulphate SO_4	2	Bicarbonate HCO_3	1
Bisulphate HSO_4	1	Hydroxyl OH	1
Sulphite SO_3	2	Perchlorate ClO_4	1
Bisulphite HSO_3	1	Chlorate ClO_3	1
Nitrate NO_3	1	Chlorite ClO_2	1
Nitrite NO_2	1	Hypochlorite ClO	1
Phosphate PO_4	3	Chromate CrO_4	2
Phosphite PO_3	3	Dichromate Cr_2O_7	2
Borate BO_3	3	Manganate MnO_4	2
Ferrocyanide $Fe(CN)_6$	4	Permanganate MnO_4	1
Ferricyanide $Fe(CN)_6$	3	Thiosulphate S_2O_3	2

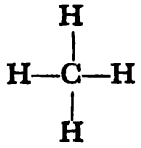
Except ammonium NH_4 which is a positive radical, the rest are negative radicals and play the part of a non-metallic element in a compound.

Structural Formulæ.—The formula of a compound may be designed graphically indicating how the atoms are linked in a molecule. For this purpose each atom of an element is assumed to possess one or more hand, which are represented by bonds or short straight lines, drawn from the symbol of the atom—the number of lines drawn corresponds to the valency of the element. The valency of hydrogen, oxygen, nitrogen, and carbon, for example, are graphically designed as :

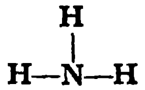
$$H- \qquad -O- \qquad -\overset{|}{N}- \qquad -\overset{|}{C}-$$

These bonds unite in pairs in chemical combination, i.e., the hand on one atom holds the hand on another ; thus the formulas for water H_2O, hydrogen peroxide H_2O_2, methane, CH_4, and ammonia, NH_3, are represented as :

$H—O—H$ $H—O—O—H$



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$



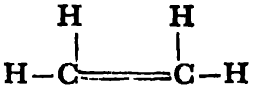
$$\begin{array}{c} H \\ | \\ H-N-H \end{array}$$

The sulphate group has 2 valency bonds so that the structural formula or sulphuric acid is :

$$H-SO_4-H$$

A pair of mutually satisfying bonds produce a single bond in a compound, as illustrated in the above compounds. In like manner, two pairs of bonds produce a double bond, and three pairs a triple bond.

A compound is said to be **saturated** when all the valencies of the constituent atoms are *fully satisfied,* and **unsaturated** when the valencies are only *partially* satisfied. Water, hydrogen peroxide, methane and ammonia, all in the above illustrations are saturated compounds. Ethylene, C_2H_4, and acetylene, C_2H_2, are unsaturated ; they are represented as :



$$\begin{array}{c} H \quad\; H \\ | \quad\;\; | \\ H-C=C-H \end{array}$$

Ethylene

$H-C\equiv C-H$

Acetylene

Ethylene contains a double bond, and acetylene a triple bond. Double and triple bonds in compounds indicate unsaturation in them.

The names of compounds.—Compounds are generally given such names as to indicate their composition. The following examples would clearly indicate the system of *chemical nomenclature,* i.e., naming of substance.

Compounds of two elements are called **binary compounds.** In naming such compounds, the name of the metal (or the more positive element) appears first, followed by the name of the non-metal (or the more negative element) with the termination **-ide.**

An **oxide** is a binary compound of an element with oxygen ; a **chloride** is a compound of an element with chlorine. In like manner the binary compounds in which one of the elements is sulphur, hydrogen, bromine, iodine, nitrogen, etc., are given the names, **sulphide, hydride, bromide, iodide, nitride,** etc., respectively, e.g.

Magnesium oxide MgO
Hydrogen sulphide H_2S
Potassium iodide KI
Magnesium nitride Mg_3N_2
Carbon tetrachloride CCl_4
Aluminium chloride $AlCl_3$
Calcium hydride CaH_2
Sodium bromide $NaBr$
Chlorine monoxide Cl_2O
Calcium carbide CaC_2

In binary compounds when an element combines with another forming more than one compound, the suffix **-ous,** or **-ic** is added to the metal (or less electronegative element) to denote the **lower** or **higher** proportion of the element respectively. Examples are :

Ferrous chloride $FeCl_2$	Ferric chloride $FeCl_3$
Stannous chloride $SnCl_2$	Stannic chloride $SnCl_4$
Mercurous oxide Hg_2O	Mercuric oxide HgO
Cuprous oxide Cu_2O	Cupric oxide CuO
Nitrous oxide N_2O	Nitric oxide NO

The prefixes **mono-, di-, tri-,** etc., are sometimes added to the non-metal or to the more negative element denoting the number of its atom in the molecule. In a series of oxides the prefix **per-** is usually, but not always, added to the one containing most oxygen, e.g.

Sodium monoxide Na_2O
Chlorine monoxide Cl_2O
Chlorine heptoxide Cl_2O_7
Phosphorus trioxide P_2O_3
Sulphur dioxide SO_2

Sodium peroxide Na_2O_2
Carbon dioxide CO_2
Chlorine dioxide ClO_2
Phosphorus pentoxide P_2O_5
Sulphur trioxide SO_3

Compounds containing three elements are called **ternary compounds** ; e.g., sulphuric acid, H_2SO_4 ; potassium chlorate, $KClO_3$; calcium carbonate, $CaCO_3$.

How to write a formula.—When an element A reacts with another element B to form a compound, the valency of A must balance that of B such that the valency of the compound as a whole is nil ; consequently valency of A must be equal and opposite to that of B, or in other words :

$$\text{total valency due to A} = \text{total valency due to B}$$

$$\text{i.e., no. of atoms of A} \times \text{valency of A} = \text{no. of atoms of B} \times \text{valency of B}$$

$$\text{or} \quad \frac{\text{number of atoms of A}}{\text{number of atoms of B}} = \frac{\text{valency of B}}{\text{valency of A}}$$

Hence, the elements A and B unite in the *simple inverse ratio of their valencies.* The relation holds equally good when radicals are involved in a chemical change.

To arrive at a formula of a compound, therefore :

(i) Write the symbols of A and B side by side—the metal or the more positive element or radical to the left and the non-metal or less positive element or radical to the right, and
(ii) Indicate by numerals their valencies at the top ; finally
(*iii*) Shift the valencies *cross-wise* to the lower right of the opposite partners. Examples are :

Compound	Symbol with valency	Formula
Aluminium	Al^3O^2	Al_2O_3
Aluminium sulphate	$Al^3SO_4{}^2$	$Al_2(SO_4)_3$
Calcium phosphate	$Ca^2PO_4{}^3$	$Ca_3(PO_4)_2$
Copper nitrate	$Cu^2NO_3{}^1$	$Cu(NO_3)_2$

When the valencies are divisible by a common factor, they are first reduced to a simple ratio and then the method is applied :

Compound	Symbol with valency	Simple ratio	Formula
Aluminium phosphate	$Al^3PO_4{}^3$	$Al^1PO_4{}^1$	$AlPO_4$
Magnesium oxide	Mg^2O^2	Mg^1O^1	MgO
Carbon dioxide	C^4O^2	C^2O^1	CO_2

Bicarbonates contain the univalent radical, HCO_3, as in $NaHCO_3$, $Ca(HCO_3)_2$ and $Fe(HCO_3)_2$, whereas the *bisulphates* contain the univalent radical, HSO_4, as in the compounds $NaHSO_4$ and $KHSO_4$.

Chemical equations.—A chemical change that matter undergoes is called a chemical reaction, and may be represented by equations involving symbols of atoms of the elements and formulæ of molecules. *A chemical equation,* therefore, *represents with the aid of symbols and formulae, a chemical reaction.* In writing a chemical equation the formulæ of

Formulæ of the following compounds further illustrate the method—the number within bracket denotes the valency.

	Oxide O (2)	Hydroxide OH (1)	Nitrate NO_3 (1)	Chloride Cl (1)	Carbonate CO_3 (2)	Sulphate SO_4 (2)	Phosphate PO_4 (3)
Sodium, Na (1)	Na_2O	$NaOH$	$NaNO_3$	$NaCl$	Na_2CO_3	Na_2SO_4	Na_3PO_4
Calcium, Ca (2)	CaO	$Ca(OH)_2$	$Ca(NO_3)_2$	$CaCl_2$	$CaCO_3$	$CaSO_4$	$Ca_3(PO_4)_2$
Aluminium, Al (3)	Al_2O_3	$Al(OH)_3$	$Al(NO_3)_3$	$AlCl_3$	—	$Al_2(SO_4)_3$	$AlPO_4$
Iron, *ic*, Fe (3)	Fe_2O_3	$Fe(OH)_3$	$Fe(NO_3)_3$	$FeCl_3$	—	$Fe_2(SO_4)_3$	$FePO_4$
Iron, *ous*, Fe (2)	FeO	$Fe(OH)_2$	$Fe(NO_3)_2$	$FeCl_2$	$Fe(CO_3)$	$FeSO_4$	$Fe_3(PO_4)_2$
Copper, *ic*, Cu (2)	CuO	$Cu(OH)_2$	$Cu(NO_3)_2$	$CuCl_2$	$CuCO_3$	$CuSO_4$	$Cu_3(PO_4)_2$
Copper, *ous*, Cu (1)	Cu_2O	—	—	$CuCl$	—	Cu_2SO_4	—
Tin, *ic*, Sn (4)	SnO_2	$Sn(OH)_4$	$Sn(NO_3)_4$	$SnCl_4$	—	$Sn(SO_4)_2$	—
Tin, *ous*, Sn (2)	SnO	$Sn(OH)_2$	$Sn(NO_3)_2$	$SnCl_2$	$SnCO_3$	$SnSO_4$	$Sn_3(PO_4)_2$
Mercury, *ic* (2)	HgO	—	$Hg(NO_3)_2$	$HgCl_2$	$HgCO_3$	$HgSO_4$	$Hg_3(PO_4)_2$
Mercury, *ous* (1)	Hg_2O	—	$Hg_2(NO_3)_2$	Hg_2Cl_2	Hg_2CO_3	Hg_2SO_4	$Hg_3(PO_4)$
Ammonium NH$_4$ (1)	—	NH_4OH	NH_4NO_3	NH_4Cl	$(NH_4)_2CO_3$	$(NH_4)_2SO_4$	$(NH_4)_2PO_4$

the reactants are connected by plus (+) signs, so also the products of the reaction—the set of the reactants being separated from the set of the products by a sign of equality (=). For example, potassium chlorate, when strongly heated, loses oxygen, and is converted into potassium chloride :

Potassium chlorate = potassium chloride + oxygen.

Replacing each name by the formulæ of the substances, the equation becomes : $KClO_3 = KCl + O_2$.

This equation is incomplete, and is said to be *unbalanced*, since 3 atoms of oxygen are contained in $KClO_3$ but only 2 are accounted for among the reaction products. This cannot be remedied by writing O_3 on the right instead of O_2, for this would mean writing an incorrect formula for oxygen. By doubling the whole expression we get : $2KClO_3 = 2KCl + 3O_2$, for a balanced equation. The equation reads thus : potassium chlorate *yields* or *produces* (which the sign of equality denotes) potassium chloride *and* (plus is read '*and*') oxygen.

Significance of a chemical equation.—A chemical equation has a *qualitative* as well as *quantitative* significance. It indicates the *nature* and the *relative amounts by weight* (and also *by volumes*, in the case of gases) of different substances involved in a chemical reaction. Let us consider the equation $C + O_2 = CO_2$.

It reads in a purely qualitative way as "carbon reacts with oxygen to form carbondioxide." But its quantitative meaning is : "one atom of carbon unites with one molecule of oxygen to yield one molecule of carbondioxide." Also

$$\begin{array}{ccccc} C & + & O_2 & = & CO_2 \\ 12 & & 32 & & 44 \end{array}$$

Expressing the atomic weights and molecular weights in grams, we may interpret the equation thus : *one gram atomic weight* of carbon unites with *one gram molecular weight* of oxygen to produce 1 *gram molecular weight* of carbondioxide. The gram atomic weight of carbon is 12 ; the gram molecular weight of oxygen is 32 and that of carbon dioxide 44. Consequently the full significance of the equation is : 12 grams of carbon unite with 32 grams of oxygen to give 44 grams of carbon dioxide. It will be established later that one gram molecular weight of any gas occupies a volume of 22.4 litres at 0°C and at a pressure of 760 mm. of mercury, i.e., at N.T.P.

$$\begin{array}{ccccc} C & + & O_2 & = & CO_2 \\ 12 & & 22.4 \text{ litres} & & 22.4 \text{ litres} \end{array}$$

The equation may, therefore, also be interpretted as : "12 grams of carbon unite with 22.4 litres of oxygen at N.T.P. to produce 22.4 litres of carbon dioxide at N.T.P."

Limitations of a chemical equation.—It cannot provide informations on the following among other points :

(i) *Energy changes*, i.e., if the reaction is exothermic or endothermic ;

(ii) *Physical state* of the reactants and the products ;

(iii) *Conditions*, e.g., temperature, pressure and catalyst, and modus operandi of the reaction.

(iv) *Rate* at which a reaction proceeds and the *time* required for its completion.

Balancing a Chemical Equation.—

A chemical equation must satisfy the following points :

(i) It should represent *a chemical change that does really take place.*

(ii) *It must balance*, i.e., it must conform to the law of conservation of mass and as such the number of atoms of *each element* on either sides of the sign of equality must be same.

(iii) All the substances appearing in equation should be represented by their *molecules*—representation of elements must also be *molecular* and not atomic, except in the case of monatomic molecules like Na and Hg etc. Usual practice is to represent *elementary gases* by their molecular formulas e.g., H_2, O_2, N_2, Cl_2, F_2, etc. *Solid elements* in the uncombined state are denoted by their symbols only, such as the metals Zn, Al, Fe, Sn, Pb, etc., and the non-metals C, Si, B, S, etc., since the number of atoms in a molecule of a solid element is sometimes though not always variable or indefinite.

Illustrations.—For simple reactions such as formation of water from its elements, first :

(i) Write a skeleton equation denoting the compounds by their molecular formulae and the elements by their symbols, as

Hydrogen + oxygen = water

$$H + O = H_2O$$

(ii) Balance the equation such that every atom on the left is found on the right of the equation, hence

$$2H + O = H_2O$$

(iii) Finally, represent every substance by its molecule, thus

$$2H_2 + O_2 = 2H_2O$$

The steps involved in arriving at a balanced chemical equation are illustrated by the following examples :

(i) Iron reacts with oxygen to yield ferric oxide.

Iron + oxygen = ferric oxide

$Fe + O = Fe_2O_3$ ... (i)

$2Fe + 3O = Fe_2O_3$ ... (ii)

$4Fe + 3O_2 = 2Fe_2O_3$ ... (iii)

Equation (iii) is the properly balanced equation.

(ii) Nitrogen combines with red-hot magnesium to produce magnesium nitride.

Magnesium + nitrogen = magnesium nitride

$Mg + N = Mg_3N_2$ ... (i)

$3Mg + 2N = Mg_3N_2$ ... (ii)

$3Mg + N_2 = Mg_3N_2$ ... (iii)

The last equation is the properly balanced one. Magnesium nitride is decomposed by water to yield magnesium hydroxide and ammonia.

Magnesium nitride + water = magnesium hydroxide + ammonia

$Mg_3N_2 + HOH = Mg(OH)_2 + NH_3$ ... (i)

$Mg_3N_2 + 6HOH = 3Mg(OH)_2 + 2NH_3$ ... (ii)

Equation (ii) is properly balanced—water is written here as HOH for convenience.

(iii) Common salt reacts with hot and strong sulphuric acid to produce sodium sulphate and hydrochloric acid.

$$\text{Common salt} + \text{sulphuric acid} = \text{sodium sulphate} + \text{hydrochloric acid}$$
$$NaCl + H_2SO_4 = Na_2SO_4 + HCl \quad \ldots \quad (i)$$
$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl \quad \ldots \quad (ii)$$

(iv) Carbon dioxide turns lime water milky due to the formation of a white precipitate of calcium carbonate and water.

$$\text{Lime water} + \text{carbon dioxide} = \text{Calcium carbonate} + \text{water}$$
$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

(v) Chalk dissolves in hydrochloric acid with an effervescence of carbon dioxide :

$$\text{Chalk} + \text{hydrochloric acid} = \text{calcium chloride} + \text{water} + \text{carbon dioxide,}$$
$$CaCO_3 + HCl = CaCl_2 + H_2O + CO_2 \quad \ldots \quad (i)$$
$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2 \quad \ldots \quad (ii)$$

Equation (ii) is properly balanced.

(vi) Ammonium chloride reacts with slaked lime giving ammonia :

$$\text{Ammonium chloride} + \text{slaked lime} = \text{calcium chloride} + \text{water} + \text{ammonia}$$
$$NH_4Cl + Ca(OH)_2 = CaCl_2 + H_2O + NH_3 \quad \ldots \quad (i)$$
$$\text{Balancing, } 2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3 \quad \ldots \quad (ii)$$

Balancing by Partial Equations.—When it is comparatively difficult to balance a chemical equation by inspection, it is advisable to arrive at the balanced equation by writing down the equation in steps—the steps representing the possible course of reaction. Each step is represented by a separate *partial equation*, and the partial equations are finally added to get the balanced equation—if and when necessary, the partial equations are multiplied by suitable integers for correctly balancing the final equation. The method is illustrated by a few examples :

(i) Hot and concentrated sulphuric acid reacts with copper turnings to produce sulphur dioxide :

Sulphuric acid decomposes into water, sulphur dioxide and oxygen. The oxygen then converts copper into copper oxide which dissolves in the sulphuric acid to give copper sulphate and water.

$$\begin{array}{rcl} H_2SO_4 & = & H_2O + SO_2 + O \\ Cu + O & = & CuO \\ CuO + H_2SO_4 & = & CuSO_4 + H_2O \\ \hline Cu + 2H_2SO_4 & = & CuSO_4 + 2H_2O + SO_2 \end{array}$$

(ii) Copper reacts with moderately strong nitric acid to yield nitric oxide.

$$\begin{array}{rcl} 2HNO_3 & = & H_2O + 2NO + 3O \\ 3Cu + 3O & = & 3CuO \\ 3CuO + 6HNO_3 & = & 3Cu(NO_3)_2 + 3H_2O \\ \hline 3Cu + 8HNO_3 & = & 3Cu(NO_3)_2 + 4H_2O + 2NO \end{array}$$

(iii) Sodium decomposes cold water to yield caustic soda and hydrogen.

$$\begin{array}{lcl} H_2O + 2Na & = & H_2 + Na_2O \\ Na_2O + H_2O & & 2NaOH \\ & & \\ 2Na + 2H_2O & & 2NaOH + H_2 \end{array}$$

(iv) Hydrogen peroxide reacts with a solution of potassium permanganate acidified with dilute sulphuric acid, evolving oxygen in the cold.

Potassium permanganate decomposes in the acid solution yielding oxygen and forming oxides of potassium and manganese which are neutralised by sulphuric acid to give salt and water. Hydrogen peroxide also breaks up releasing oxygen. The equation may be built up as follows :

$$2KMnO_4 = K_2O + 2MnO + 5O$$
$$K_2O + H_2SO_4 = K_2SO_4 + H_2O$$
$$2MnO + 2H_2SO_4 = 2MnSO_4 + 2H_2O$$
$$5H_2O_2 = 5H_2O + 5O$$
$$5O + 5O = 5O_2$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

(v) Potassium iodide reacts with hot and concentrated sulphuric acid, evolving violet vapours of iodine :

$$2KI + 2H_2SO_4 = 2KHSO_4 + 2HI$$
$$H_2SO_4 = H_2O + SO_2 + O$$
$$2HI + O = H_2O + I_2$$

$$2KI + 3H_2SO_4 = 2KHSO_4 + 2H_2O + SO_2 + I_2$$

(vi) Sulphur dioxide reduces a solution of potassium dichromate acidified with dilute sulphuric acid—the colour of the solution changing from orange yellow to green. Potassium dichromate breaks up giving oxygen and oxides of potassium and chromium which dissolve in acid to produce salt and water. The liberated oxygen converts sulphur dioxide into sulphur trioxide which with water gives sulphuric acid.

$$K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3O$$
$$K_2O + H_2SO_4 = K_2SO_4 + H_2O$$
$$Cr_2O_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O$$
$$3SO_2 + 3O = 3SO_3$$
$$3SO_3 + 3H_2O = 3H_2SO_4$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

(vii) Chlorine oxidises sulphurdioxide water into sulphuric acid.

$$Cl_2 + H_2O = 2HCl + O$$
$$SO_2 + O = SO_3$$
$$SO_3 + H_2O = H_2SO_4$$

$$Cl_2 + 2H_2O + SO_2 = 2HCl + H_2SO_4$$

(viii) Ozone liberates iodine from potassium iodide solution :

$$O_3 = O_2 + O$$
$$2KI + O = K_2O + I_2$$
$$K_2O + H_2O = 2KOH$$

$$2KI + O_3 + H_2O = 2KOH + O_2 + I_2$$

(ix) Sulphur dioxide reduces cupric chloride into cuprous chloride.

$$2CuCl_2 = 2CuCl + 2Cl$$
$$H_2O + SO_2 + 2Cl = 2HCl + SO_3$$
$$SO_3 + H_2O = H_2SO_4$$

$$2CuCl_2 + SO_2 + 2H_2O = H_2SO_4 + 2HCl + 2CuCl$$

Exercises

✓1. What do you understand by the terms *atom*, *molecule*, *valency* ?

Write down the formulæ, and calculate the molecular weight of the following compounds : copper sulphate, calcium bicarbonate, ferric sulphate, ferrous sulphate, sodium bisulphate, ammonium carbonate, stannic chloride, mercurous chloride, aluminium sulphate, ferric hydroxide.

2. Write down the equations for the following reactions :
   (a) iron is heated in a current of chlorine.
   (b) the action of zinc on copper sulphate solution,
   (c) the burning of phosphorus in air,

(d) a knife blade is dipped into copper sulphate solution,
(e) the combination of phosphorus and iodine,
(f) the decomposition of limestone by heat,
(g) the action of dilute sulphuric acid on iron filings,
(h) the action of heat on potassium chlorate.

Translate the following equations into symbols :

(i) limestone + hydrochloric acid = calcium chloride + water + carbon dioxide,
(ii) barium chloride + sodium sulphate = barium sulphate + sodium chloride,
(iii) sodium chloride + sulphuric acid = sodium bisulphate + hydrochloric acid,
(iv) silver nitrate + sodium chloride = silver chloride + sodium nitrate,
(v) sodium + water = caustic soda + hydrogen,
(vi) sulphuric acid + iron = ferrous sulphate + hydrogen,
(vi calcium oxide + water = slaked lime,
(vii ferric oxide + aluminium = aluminium oxide + iron,
(i sodium hydrixode + hydrochloric acid = sodium chloride + water,
(lead nitrate = lead monoxide + nitrogen dioxide + oxygen.

✓4. Explain why both sides of a chemical equation must balance. Balance the follow equations :

(a) $Fe_2O_3 + CO = Fe + CO_2$; (b) $Ca + H_2O = Ca(OH)_2 + H_2$,
(c) $KClO_3 = KCl + O_2$; (d) $Sn + Cl_2 = SnCl_4$
(e) $PbS + H_2O_2 = PbSO_4 + H_2O$; (f) $H_2 + O_2 = H_2O$.

✓5. What information does the equations : (a) $2H_2 + O_2 = 2H_2O$; (b) $C + O_2 = CO_2$, convey to you ? Balance the following equations :

(i) $Fe + HCl = FeCl_2 +$; (ii) $Ca(OH)_2 + HCl = CaCl_2 +$;
(iii) $P + O_2 =$; (iv) $Pb(NO_3)_2 = PbO + NO_2 +$;
(v) $CuSO_4 + Fe = FeSO_4 +$; (vi) $Al + Cl_2 = AlCl_3$.

What is a chemical equation ? On what principles is it formed and what does it convey ? What information it does not convey ? *U. P. Board, '31*

7. What are the essential characteristics of a chemical equation ? What are its drawbacks ? Balance the following equations.

(i) $KMnO_4 + H_2SO_4 + H_2O_2 = K_2SO_4 + MnSO_4 + H_2O + O$.
(ii) $As_2O_3 + SnCl_2 + HCl = SnCl_4 + As + H_2O$.
(iii) $C_2H_2 + O = H_2O + CO_2$.
(iv) $Cu + HNO_3 = Cu(NO_3)_2 + H_2O + NO$.

8. Discuss the importance of a chemical equation. Write equations for the following reactions : (a) action of chlorine on caustic soda solution, (b) action of nitric acid on copper, (c) action of ozone on potassium iodide solution, (d) action of caustic soda solution on phosphorus, and (e) action of heat on barium carbonate.

IV

ACIDS, BASES, AND SALTS

Acids.—It is found that certain properties are shared by all acids ; all acids, for example, have a sour taste—the very name acid comes from a Latin word meaning sour. **Acids turn blue litmus red ;** thus, when a few drops of blue litmus solution are added to a little dilute sulphuric acid in a test tube, the entire solution turns red. Many acids, acting on certain metals, would liberate hydrogen gas.

When a little dilute sulphuric acid, for example, is added to a piece of granulated zinc in a test tube, there is a brisk evolution of hydrogen gas. The gas may be burnt in a jet with a pale blue flame. The above properties are not, however, sufficiently precise to define an acid.

An **acid** *is a compound containing one or more* **replaceable** *hydrogen atoms which may be partially or wholly replaced by a metal forming a salt, when acted upon by certain metals, metallic oxides, and hydroxides.*

Thus, iron reacts with dilute sulphuric acid, producing ferrous sulphate and liberating hydrogen ; ferrous sulphate is the salt of sulphuric acid.

$$Fe + H_2SO_4 = FeSO_4 + H_2$$

Zinc oxide reacts with sulphuric acid producing zinc sulphate (which is a salt of sulphuric acid), and water :

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O$$

Calcium hydroxide dissolves in nitric acid forming calcium nitrate and water ; calcium nitrate is the salt of nitric acid.

$$Ca(OH)_2 + 2HNO_3 = Ca(NO_3)_2 + 2H_2O$$

The acids are divided into two classes : the **hydracids** and the **oxyacids.** The hydracids do not contain oxygen—besides hydrogen they contain another non-metallic element (or radical) only.

They take the affix **-ic** and the prefix **hydro-** in their names e.g., hydrofluoric acid, HF ; hydrochloric acid, HCl ; hydrobromic acid, HBr ; hydriodic acid, HI ; Hydrocyanic acid, HCN.

The **oxyacids** contain oxygen—besides containing both hydrogen and oxygen they contain another element (or radical).

The ending **-ic** or **-ous** are used to denote acids containing more or less oxygen respectively, e.g.,

Sulphuric acid H_2SO_4	Sulphurous acid H_2SO_3
Nitric acid HNO_3	Nitrous acid HNO_2
Chloric aicd $HClO_3$	Chlorous acid $HClO_2$
Phosphoric acid H_3PO_4	Phosphorous acid H_3PO_3

The oxyacids containing less oxygen than the **-ous** acid, have the affix **-ous** and the prefix **hypo-** in their names. The oxyacids having more oxygen than the **-ic** acid, carry the affix **-ic** and the prefix **per-** in their names, e.g.,

Phosphorous acid H_3PO_3	Hypophosphorous acid H_3PO_2
Chlorous acid $HClO_2$	Hypochlorous acid HClO
Chloric acid $HClO_3$	Perchloric acid $HClO_4$

The common **mineral acids** are hydrochloric acid, HCl, sulphuric acid H_2SO_4, and nitric acid, HNO_3.

Thioacids.—Thio acids are derived from oxyacids by partial or complete replacement of oxygen by sulphur. Thiosulphuric, $H_2S_2O_3$, may be considered as derived from sulphuric acid H_2SO_4, by the replacement of one oxygen atom by one sulphur atom. Sodium thiosulphate, $Na_2S_2O_3$, $5H_2O$, also called *hypo*, is the well-known salt of thiosulphuric acid. Cyanic acid is HCNO ; thiocyanic acid is HCNS ; potassium thiocyanate, also called potassium sulphocyanide, is KCNS.

Salts.—The term **salt** is commonly applied to sodium chloride NaCl, also known as *common salt.* But the term salt in chemistry refers to the products formed by the displacement of **replaceable**

hydrogen atom of acids by metals—**normal salts** are produced by the complete replacement, and **acid or bisalts** by **partial** replacement of the replaceable hydrogen atoms. A salt is, therefore, a compound in which the replaceable hydrogen atoms of an acid have been replaced by a metal. Thus, sodium sulphate Na_2SO_4, is a salt, since it is sulphuric acid H_2SO_4, in which two hydrogen atoms have been replaced by two atoms of sodium. Similarly, sodium chloride NaCl, is a salt, because it is hydrochloric acid HCl, in which the hydrogen atom has been replaced by sodium. Salts of hydracids end in **-ide.**

Acid	Sodium salt
Hydrochloric acid HCl	Sodium chloride NaCl
Hydrobromic acid HBr	Sodium bromide NaBr
Hydriodic acid HI	Sodium iodide NaI
Hydrofluoric acid HF	Sodium fluoride NaF
Hydrocyanic acid HCN	Sodium cyanide NaCN

The termination **-ite** is affixed to the name of the salt of any **-ous** acid, and **-ate** to the salt of any **-ic** acid.

Acid	Sodum salt
Sulphuric acid H_2SO_4	Sodium sulphate Na_2SO_4
Sulphurous acid H_2SO_3	Sodium sulphite Na_2SO_3
Nitric acid HNO_3	Sodium nitrate $NaNO_3$
Nitrous acid HNO_2	Sodium nitrite $NaNO_2$
Carbonic acid H_2CO_3	Sodium carbonate Na_2CO_3
Phosphoric acid H_3PO_4	Sodium phosphate Na_3PO_4
Hypochlorous acid HOCl	Sodium hypochlorite NaOCl
Chlorous acid $HClO_2$	Sodium chlorite $NaClO_2$
Chloric acid $HClO_3$	Sodium chlorate $NaClO_3$
Perchloric acid $HClO_4$	Sodium perchlorate $NaClO_4$

Salts may contain metals which exhibit variable valency. In such cases, when the metal shows the lower valency, the metallic portion of the name ends in **-ous,** and when it exhibits higher valency, it takes the affix **-ic,** e.g.

Ferrous sulphate $FeSO_4$	Ferric sulphate $Fe_2(SO_4)_3$
Stannous chloride $SnCl_2$	Stannic chloride $SnCl_4$
Cuprous chloride CuCl	Cupric chloride $CuCl_2$

Sodium hydrogen sulphate, $NaHSO_4$, is an acid salt of sulphuric acid ; it still contains replaceable hydrogen, and a solution of it turns blue litmus red. It is also called *sodium bisulphate ;* it contains the univalent bisulphate radical HSO_4.

The formula for *sodium bicarbonate* is $NaHCO_3$; it is an acid salt of carbonic acid H_2CO_3. The bicarbonates contain the bicarbonate radical HCO_3, which is univalent. Calcium bicarbonate has the formula $Ca(HCO_3)_2$.

Bases.—A base is a compound (the oxide or hydroxide of a metal) which reacts with an acid to produce a salt and water only.

(i) Cupric oxide dissolves in sulphuric acid, producing cupric sulphate and water : $CuO + H_2SO_4 = CuSO_4 + H_2O$

(ii) Sodium hydroxide reacts with sulphuric acid, forming sodium sulphate and water : $2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$

The acid salt sodium bisulphate is formed when lesser amount of sodium hydroxide is used : $NaOH + H_2SO_4 = NaHSO_4 + H_2O$.

(iii) Aluminium oxide reacts with sulphuric acid producing aluminium sulphate and water : $Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O$

(iv) Ferric oxide dissolves in hydrochloric acid, forming ferric chloride and water : $Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$

An oxide of a metal, if soluble in water produces **hydroxide.**

$Na_2O + H_2O = 2NaOH$ (sodium hydroxide)
$K_2O + H_2O = 2KOH$ (potassium hydroxide)
$CaO + H_2O = Ca(OH)_2$ (calcium hydroxide).

The hydroxides of metals are compounds of metals with the hydroxyl group, OH ; the metallic hydroxides are bases.

Soluble hydroxides are called alkalis.—The term **alkali** is, therefore, applied to bases which are soluble in water. In addition to their property of forming salts with acids, the alkalis possess the following properties : (i) *their solutions turn red litmus solution blue ;* (ii) *their solutions have a soapy feel when rubbed between the fingers.*

Such substances as sodium hydroxide (also called *caustic soda*), potassium hydroxide (also called *caustic potash*), and calcium hydroxide which are soluble in water, are called alkalis. A solution of calcium hydroxide is known as *lime water.*

Insoluble hydroxides, such as aluminium hydroxide $Al(OH)_3$ and ferric hydroxide $Fe(OH)_3$, are not alkalis, but they are bases ; and consequently, *all bases are not alkalis, but all alkalis are bases.*

Ammonia NH_3 dissolves in water producing ammonium hydroxide which is alkaline : $NH_3 + H_2O = NH_4OH$ (ammonium hydroxide).

Exercises

1. Write down the names and formulæ of the sodium salts of the following acids : nitrous, hypophosphorous, perchloric, hypochlorous, carbonic, sulphurous, hydroiodic, and sulphuric.

Name three most important mineral acids.

2. What is meant by a base ? Is there any difference between a base and an alkali ? Is sodium carbonate a base ?

Explain what happens when :

(*a*) water is slowly added to a lump of quick lime,
(*b*) dilute sulphuric acid acts on granules of zinc,
(*c*) concentrated hydrochloric acid acts on ferric oxide,
(*d*) caustic soda solution is slowly added to some hydrochloric acid which has been coloured red with litmus solution,
(*e*) strong hydrochloric acid acts on tin,
(*f*) dilute hydrochloric acid acts on sodium carbonate.

3. Define the terms *acid, base,* and *salt.* What are the properties of an acid ? A solution turns blue litmus red. Is this a sufficient inormation to call the solution an acid ?

What information does this equation—

$$NaOH + HCl = NaCl + H_2O$$

convey to you ?

V

COMMON LABORATORY PROCESSES

Matter consisting of one substance only is said to be *pure.* Thus, water is a pure substance, since it contains nothing but water. A sample of muddy water, on the other hand, is impure, since it contains other things besides water. In order to study the properties of a substance it must be obtained in the pure state. A specimen of a pure substance is simply a collection of identical molecules.

Solution.—When a little common salt is shaken in a test tube with water, it seems to disappear, giving a **homogeneous** i.e., a uniform mixture. No trace of the salt can be found, when the liquid is examined under the most powerful microscope. The common salt is said to be dissolved in the water, and a **solution** has been formed. When, however, the common salt is added in successive small amounts to water, and the mixture is stirred, the salt dissolves *up to a certain point* only, forming a uniform mixture ; after this the salt no longer passes into solution, but settles down unchanged. There is thus a limit to the amount of salt that may be dissolved by a given quantity of water at a particular temperature. The composition of a solution is *variable*, because the quantity of salt that dissolves in a given amount of water may vary. *The composition of a solution may vary within certain limits, but that of a compound is fixed and definite and can not vary.*

A **solution** *is a homogeneous mixture of two or more substances which has the same composition and physical properties in every part,* the composition of the mixture being, however, capable of variation within certain limits. The different substances are uniformly and intimately mixed with each other in a solution.

The common salt that has dissolved in the water, still exists as salt and may be easily recovered by driving off the water by boiling the solution in an *evaporating dish* or *basin, usually* made of porcelain. When all the water is driven off as steam, a white deposit of common salt is left in the dish ; a deposit such as this, is called a residue. The solution is said to have been evaporated to dryness, and the process is known as **evaporation.** The solution is evaporated on a *water-bath* (fig. 10) to avoid any loss by spirting.

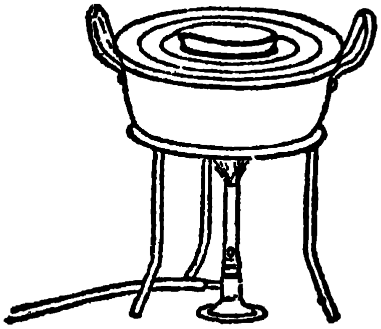


Fig. 10

A solution may be a solid, liquid, or a gaseous mixture. Air which is a mixture of nitrogen and oxygen mainly, is a gaseous solution. The addition of alcohol to water produces a homogeneous mixture of two different chemical substances uniformly and intimately mixed with each other ; this is a liquid solution.

It is obvious that a solution must consist of at least two substances—the substance which has dissolved and that which dissolved it. The dissolved substance is called the **solute,** and the dissolving medium is called the **solvent.** It may, therefore, be written :

solution = solute + solvent.

The solute distributes itself uniformly throughout the solvent without having any tendency to settle on standing. A solution is said to be **dilute** or **concentrated** according as the amount of solute is relatively small or large. Sometimes the terms *weak* or *strong* are used in a similar sense.

A much more precise meaning is conveyed by what is called **concentration** of the solution, which is generally expressed as the number of grams of dissolved substance per 100 grams of the solvent.

Quite commonly when one substance dissolves into another, it is a convention to designate as the *solvent* that component which is present in larger proportion, and to name the other component the *solute*. But this designation is rather arbitrary, particularly when two liquids are miscible in all proportions.

Water is a very common solvent. But it must not be assumed that water is the only solvent. Many substances like rubber, oils, grease, wax, tar, etc., are not soluble in water. Tar, oil and grease are, however, readily soluble in petrol, and hence the use of petrol in the dry cleaning of dirty clothes. Varnish is a solution of shellac in methylated spirit. Petrol, benzene, methylated spirit, and turpentine are a few solvents of everyday use. Alcoholic solutions of medicines are called **tinctures** or **spirits,** e.g., tincture of iodine ; spirit of camphor.

It must be remembered that when a solution is referred, it is not necessarily a solution of a solid in a liquid. Gases may dissolve in liquids ; carbon dioxide, for example, is appreciably soluble in water—'aerated waters' such as lemonades and soda waters are but aqueous solutions of carbondioxide under pressure. Some liquids will dissolve each other. Alcohol dissolves in water in all proportions. Gases always dissolve each other in all proportions. The air is a gaseous solution. Many solids dissolve some other solids producing a homogeneous mixture of solids, referred to as *solid solutions*. When gold is melted and some silver is added, the silver dissolves in the gold, and on cooling, a solid solution is produced. Solids may also dissolve gases ; palladium dissolves hydrogen forming a solid solution.

There are may substances which do not dissolve in water ; they are said to be insoluble. Thus, chalk, glass, stone, most metals, sand, cotton, paper, etc., are but few of the insoluble materials.

Filtration.—When a mixture of some sand and common salt is shaken with water, the salt goes into solution while the sand particles remain in suspension. On standing, however, the sand, being heavier, slowly settles down to the bottom, finally leaving a clear liquid at the top, sometimes called the supernatant liquid. The settled solid is known as the **sediment,** and this process of settling down of heavy solids is referred to as **sedimentation.**

The clear supernatant liquid at the top may be carefully poured off without disturbing the settled solids at the bottom. This process of pouring off the supernantant liquid without disturbing the sediment is known as **decantation.**

When a sample of turbid muddy water is allowed to stand undisturbed for some time, the suspended particles of sand and clay, etc., slowly settle and sink to the bottom, and consequently the turbidity clears.

But like such materials as sand and clay, there are many insoluble solids which do not settle quickly. Their separation is effected by filtration.

Filtration *is a process in which a liquid is separated from insoluble solids by pouring the mixture (of liquid and insoluble substance) into some porous material, such as filter paper, cloth, etc., which allows the liquid to pass through but retains the suspended solid particles.*

In the laboratory a special blotting paper, known as filter paper, is usually employed as the porous medium. A circular piece of filter paper is folded into quarters, and then opened out with three quarters on one side and one on the other (fig. 11). It is then fitted in a glass

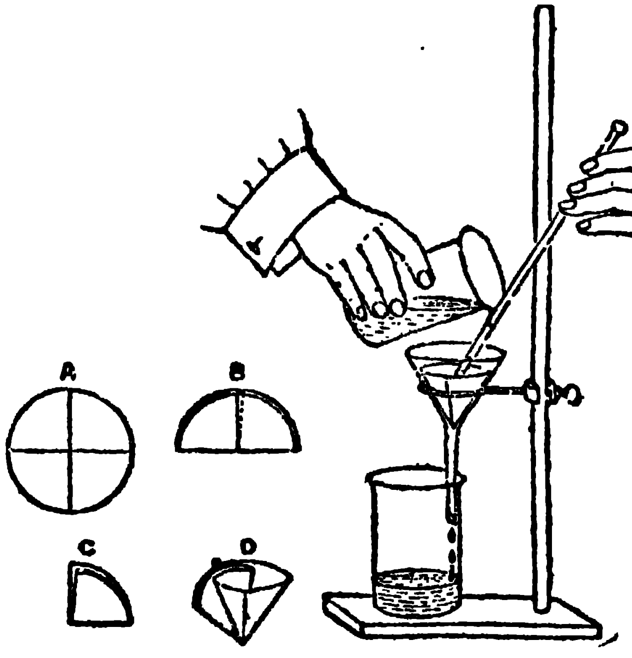


Fig. 11

funnel, which may be held in a filter stand. On pouring the mixture of liquid and insoluble solid into the filter paper, the liquid passes through the pores of the paper and is collected in a beaker below—the suspended solid particles are too large to pass through the pores and are held back.

The liquid passing through the filter paper is called the **filtrate** and the solid retained on the filter paper is called the **residue.** Hot solutions filter more rapidly than cold ones. Figure 12 is a hot filter. Filtration under reduced pressure is a much quicker process.

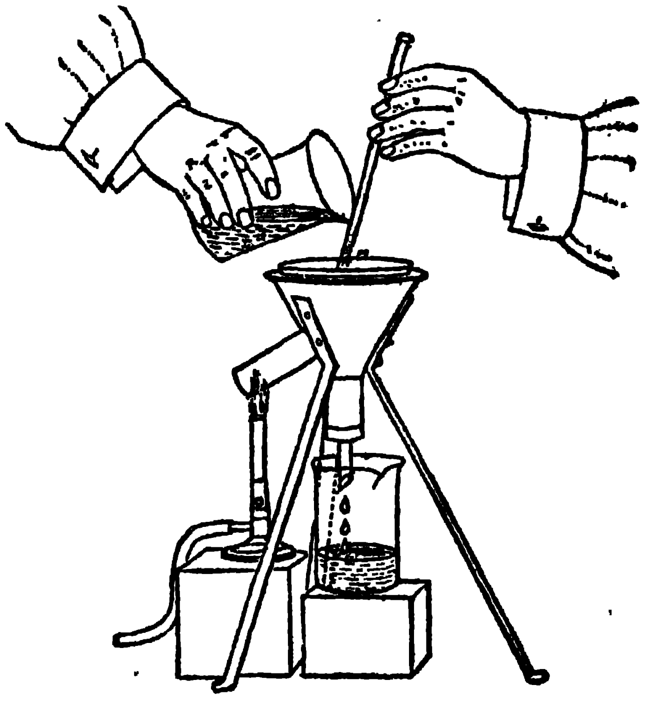


Fig. 12

For quick filtration in the laboratory a funnel with a perforated disc, usually a Buchner funnel, is fitted into a closed flask in which a partial vacuum is created by a water suction pump. The filter paper is laid on the disc. The atmospheric pressure acting on the surface of the liquid in the funnel forces it through the filter paper into the flask (fig. 13).

Vacuum filters used in industrial processes act on the same principle.

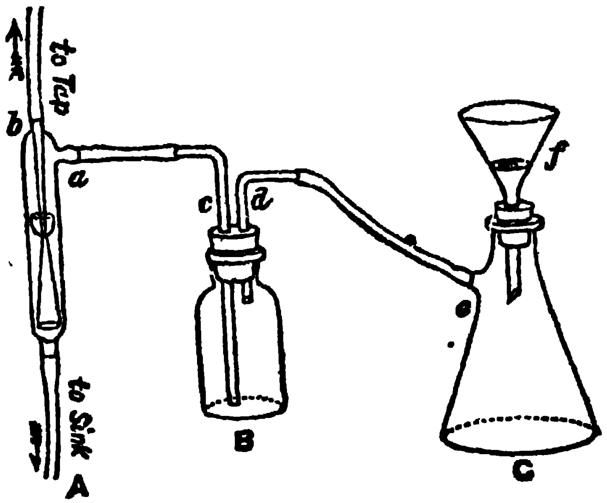


Fig. 13

To separate a mixture of Chalk and common salt—Chalk, also called calcium carbonate, is insoluble in water; salt dissolves. Some of the mixture is stirred with water, using a glass rod, in a beaker, and poured in thin stream into the filter paper fitted in a glass funnel and moistened with water—care being taken that none comes over the top of the paper. The filtrate is collected in an evaporating dish, and evaporated over a wire gauge on a tripod stand. The common salt is left as a residue after evaporation.

The chalk is retained on the filter paper. Several portions of water are poured over the chalk to wash it free from any adhering salt solution. The filter paper in the funnel is then dried, and the residue of chalk is separated from the filter paper.

Sand (insoluble in water) and common salt can be separated in the same way from their mixture.

To separate gun powder into its constituents.—Gunpowder is an intimate mixture of about 6 parts of potassium nitrate, one part sulphur, and one part charcoal. Of these, only potassium nitrate, also called *nitre* or *saltpetre*, is soluble in water. Sulphur dissolves in carbon disulphide, but charcoal is insoluble in this reagent.

To obtain all three constituents from a given sample of gun powder, some of it is shaken with sufficient quantity of carbon disulphide to dissolve out all the sulphur, and filtered. The filtrate is collected in an evaporating dish, and allowed to evaporate **by itself.** Lemon-yellow crystals of sulphur will deposit in the dish. Carbon disulphide being *very inflammable*, should be kept away from flames.

The residue of nitre and charcoal is held back on the filter paper; this is dried to remove any adhering carbon disulphide. The residue is then separated from the filter paper and stirred with sufficient **hot** water to dissolve out the nitre and filtered.

The filtrate is collected in a basin, and evaporated to dryness, when the potassium nitrate is obtained as a colourless residue. The charcoal is left as a black residue on the filter paper; it is washed with water to free from nitre solution, dried in a steam oven and separated from the filter paper.

GUNPOWDER

A mixture of nitre, charcoal and sulphur. Add carbon disulphide ; shake ; filter.

Nitre and charcoal ; dry ; treat with boiling water ; filter.

Filtrate

Solution of sulphur ; evaporate ; residue yellow crystals of sulphur.

Residue

Charcoal ; wash with water ;

Filtrate

Solution of nitre ; evaporate ;

Asbestos, sand, cotton, glasswool, etc. are often used as filtering medium.

Solution of solids in liquids.—The most important solutions are formed by dissolving solids in liquids. As already mentioned, there is a limit to the amount of solute that may dissolve in a given quantity of water at a particular temperature. When, for example, sugar is added gradually in successive small amounts to water, and stirred, it dissolves in water up to a certain extent only ; after this, the sugar no longer passes into solution but simply settles out unchanged. The solution is then said to be **saturated** with sugar at the temperature of the experiment.

A solution is said to be saturated at a given temperature when it can exist unchanged in contact with the excess of the undissolved solute.

A saturated solution, therefore, contains the maximum amount of a solute in the dissolved state at a given temperature ; if the solution contains less, it is said to be **unsaturated.** An unsaturated solution, therefore, dissolves more of the solute when brought in contact with it.

A solution is said to be **super-saturated,** i.e., **more than saturated,** when it somehow holds more solute than what should be present in its saturated solution at a given temperature.

Sometimes it happens that when a *hot* saturated solution is *cooled* in absence of any dust or undissolved solute, the excess of the solute (i.e., the amount of substance which can no longer be held in solution in the lower temperature) is not thrown out of the solution ; the solution is then said to be *super-saturated.* Such super-saturated solutions are very unstable. Stirring and scratching the wall of the container or the presence of a little dust throws the excess solute out of the solution. An infallible method of making a super-saturated solution throw the excess solute is to drop in a small crystal of the solute into the solution ; the added crystal provides a centre about which the excess solute separates.

To make a super-saturated solution of hypo.—A super-saturated solution of sodium thiosulphate, $Na_2S_2O_3.5H_2O$ also called hypo, is very easily obtained by simply heating the solid substance. Hypo contains combined water known as its water of crystallisation, and when heated it dissolves in this water.

A large test tube is half filled with crystals of 'hypo', and its neck plugged with cotton wool to prevent the entrance of dust. The tube is then heated in a beaker of boiling water. The hypo melts in its own water of crystallisation and forms a super-saturated solution. When this solution is carefully cooled, this remains liquid, and no hypo is deposited—and this is in spite of the fact that initially the entire amount of hypo was present as dry crystals. On removing the plug and putting into the liquid a small crystal of hypo, the liquid at once begins to solidify.

Liquid honey is a super-saturated solution of sugar mainly ; on long standing the sugar will crystallise.

Solubility.—Solubility depends much upon the chemical nature of the solute and of the solvent. Common salt, for example, is soluble in water, but not in alcohol ; while in the same solvent water, hypo is much more soluble than the common salt. Substances differ atly in the extent to which they dissolve in water.

Increasing the surface area of solid by powdering hastens its solution greatly. An *agate mortar and pestle* (fig. 14) is generally used to powder a solid in the laboratory.

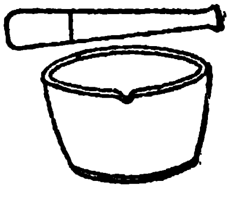


Fig. 14

The solubility of a solid generally increases with the increase of temperature. The solubility of different solutes may not increase to the same extent with the rise in temperature ; the solubility of nitre, for example, increases much more rapidly with temperature than that of the common salt. The solubility of some substances, such as sodium sulphate, first increases and then decreases with temperature. For every temperature there is a maximum saturation solubility. It is, therefore, convenient to have some standard to compare the extent of solubilities of different substances in solvents.

The **solubility** *of a solid in a solvent at a given temperature is the number of grams of the solid which dissolves in* 100 *grams of the solvent to give a saturated solution at that temperature.*

Let x gm. of a solute saturate y gm. of a solvent at t°C, then its solubility at t°C $= 100\,x/y$.

If m gms. of solute be present in w gms. of its saturated solution at t°C, then its solubility at t°C $= 100\,m/(w\text{-}m)$.

When it is mentioned that the solubility of common salt in water is 36.0 at 20°C, it means that 100 gm. (or 100 c.c., since 1 c.c. of water weighs, very nearly, 1 gm.) of water will just dissolve 36.0 gm. of common salt at 20°C to yield a saturation at the said temperature.

Determination of solubility of nitre.—Suppose it is required to determine the solubility of potassium nitrate, also called nitre, in water at the temperature of the room i.e., it is required to find out the weight of potassium nitrate which will just saturate 100 gm. of water at the temperature of the laboratory.

For this, a saturated solution of potassium nitrate is first prepared by stirring some powdered potassium nitrate with water in a test tube at the room temperature, so that some excess solid is left over at the bottom of the tube—a fact that ensures that the solution is saturated.

The saturated solution is then filtered into an evaporating dish or basin, which has been weighed previously. The whole is then weighed again. The contents of the dish are then carefully evaporated to dryness over a small flame or on a water-bath—care must be taken to avoid loss of salt by spiriting, and to ensure that the residue is perfectly dry at the end of heating. The dish with the dry salt is then cooled in a desiccator and weighed again.

Let	Weight of dish	a gm.
	Weight of dish + nitre solution	b gm.
	Weight of dish + nitre	c gm.
∴	weight of nitre	(c−a) gm.
∴	weight of water	(b−c) gm.

i.e., (b−c) gm. of water dissolves (c−a) gm. of nitre

∴ 100 gm. of water dissolve $\frac{(c-a)}{(b-c)}\times 100$ gm. of nitre, which is, therefore, the solubility of nitre.

Solubility of common salt can be similarly determined.

The experiment may be repeated to determine the solubility at different temperatures, using a thermostat, which is an arrangement to obtain constant temperatures. The following results for potassium nitrate and sodium sulphate (Glauber's salt) are illustrative.

Temperature	0°	10°	20°	40°	60°	80°	100°
Potassium nitrate	13.3	20.9	32	64	110	169	246
Glauber's salt	5.0	9.0	19.4	49	45	44	42

The solubilities in grams per 100 gm. of water, are plotted against the temperatures. (fig. 15).

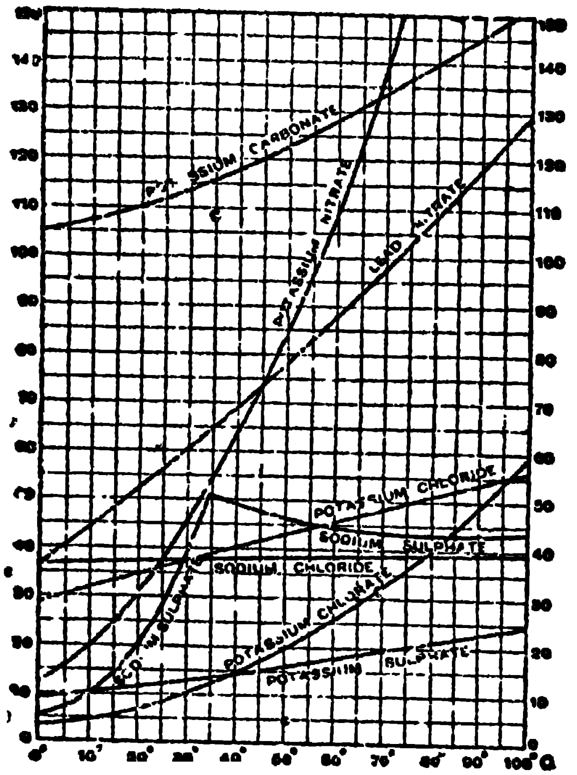


Fig. 15

Solubility curves.—The dependence of solubility on temperature is represented graphically by means of **solubility curves,** in which the abscissae represent the temperatures, and the ordinates the solubilities. The figure 15 gives the solubility curves of some salts in water. It is seen that the solubility curves of different salts are different in type. The solubility of some salts, e.g., potassium nitrate, increases rapidly with temperature, and hence their curves slope upwards. The curve for common salts is very nearly horizontal, showing that it is hardly* more soluble in hot water than in cold. Some salts, such as sodium sulphate, become less soluble at high temperatures.

The solubility curves, therefore, give directly the solubility of a substance at a given temperature, and also help us to make a comparative idea of the solubilities of different substances.

(The solubility curve also tells us how much of the substance will be thrown out of solution, when its saturated solution at a higher temperature is cooled to any lower temperature.) Thus the solubility curve tells us that the solubility of nitre is 110 at 60°C, and that at 20°C is 32, and consequently when a saturated solution containing 100 gm. of water is cooled from 60° to 20°, the amount of nitre deposited will be 110—32 = 78 gm.

The curves also give information as to which will deposit first when a mixed solution is subjected to evaporation. Thus, when a solution containing potassium chloride and potassium chlorate in equal proportions, is being evaporated at 50°C, the curves tell us that the solution gets saturated with potassium chlorate first as its solubility is less than that of potassium chloride. Hence the potassium chlorate will be deposited first, and until the solution also gets saturated with potassium chloride.

Freezing mixture.—When any soluble substance is added to water, the freezing point is lowered. If a dilute solution of common salt is cooled, the temperature falls until pure ice begins to separate just below 0°C. The removal of water as ice increases the concentration of the solution, so that the freezing point falls progressively, since the lowering of freezing point is proportional to the concentration of the solution. A point is, however, soon reached when the water left in the solution is only just sufficient to keep the salt in solution. On further cooling, both ice and salt separate together and the temperature remains constant until the solidification is complete. This minimum temperature at which the ice and salt separate *en masse* is called the *eutectic temperature* and the mixture of ice and salt separating is known as *eutectic mixture*. The eutectic temperature of ice and common salt is −21.2°C. So if ice and salt are mixed in the proportion required to form eutectic mixture, the temperature falls to −21.2°C, and ice and salt form what is called a *freezing mixture*. The temperature of a freezing mixture of ice and calcium chloride in the ratio 1 : 2 falls to −55°C.

Solutions of gases in liquids.—Liquids can dissolve gases. Carbon dioxide is fairly soluble in water. Air is slightly soluble in water—the dissolved air supports the life of aquatic animals.

Some tap water is taken in a large beaker, and a test tube full of water is inverted over the stem of a funnel placed in the beaker, as shown in the figure 16. The beaker is placed on a wire gauze over a tripod stand ; on heating bubbles of gas are collected in the test tube ; such water therefore contains dissolved gas. The dissolved gas in ordinary water is mainly air.

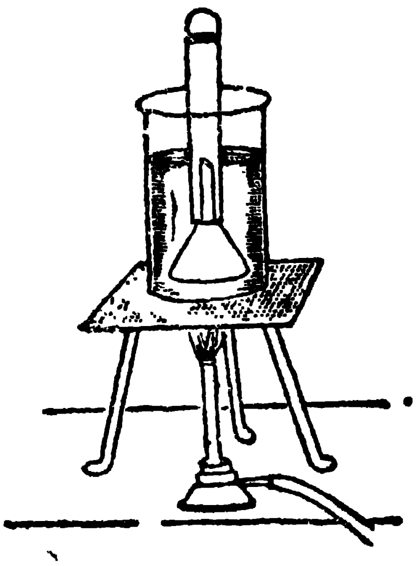


Fig. 16

Unlike solids the solubility of a gas in liquids decreases with rise in temperature. The solubility of gas, however, increases with pressure. Soda-water is a solution of carbon dioxide in water under pressure ; when a soda-water bottle is opened the dissolved gas escapes in bubbles as *effervescence* owing to the reduction of pressure.

Solution of liquids in liquids.—Alcohol dissolves in water in all proportions, i.e., it is completely miscible. But there are liquids such as water and mercury, which are completely immiscible. Some liquids are partially miscible. Thus, when ether is gradually added to water, it at first dissolves but up to a small extent only ; after which two distinct layers separate—the top layer is ether with a trace of water dissolved in it, while the bottom layer is mainly water containing, however, a little dissolved ether. The two layers can be separated by a separating funnel (Fig. 17).

When the two layers of ether and water are shaken with a little iodine in a separating funnel, it is found that the iodine is shared between the two liquids, but most of it is dissolved out by the ether, as is evident from the darker brown colour of the ether layer. Ether may, therefore, be used to extract iodine from its solution in water. Carbon disulphide also extracts iodine—the solution in this case assumes a beautiful violet colour ; the carbon disulphide forms the bottom layer, as it is heavier than water.

The method is widely used for extracting many substances from their solutions in water.

Suspensions and emulsions.—When such substances as particles of clay, flour, etc., which are insoluble in water, are shaken with water and allowed to stand—the solid particles slowly settle down to the bottom. Such mixtures are obviously heterogeneous and are called suspensions. When a liquid is suspended in minute drops into another liquid, the mixture is called an emulsion. Milk is an emulsion of butterfat, etc., in water.

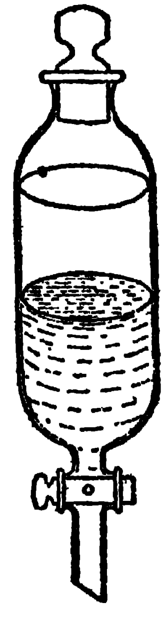


Fig. 17

Distillation.—When an aqueous solution is evaporated it is found that the water escapes as steam ; the steam may be condensed back into water by cooling.

Distillation is the process of converting a volatile liquid into its vapour by boiling, and then condensing the vapour back to the liquid state by the application of cold :

The process is useful in separating a volatile liquid from a non-volatile solid in solution or suspension.

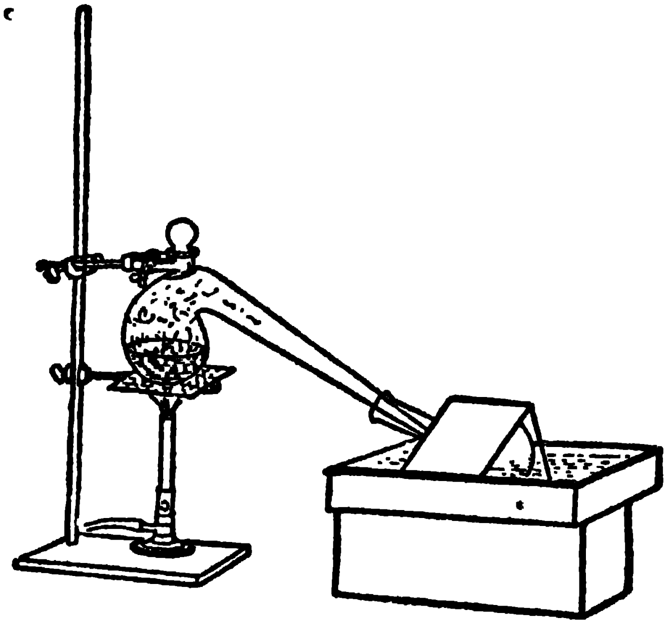


Fig. 18

A sample of muddy water may be purified by distillation. The water is poured into the retort through an opening at the top, called the tubulure. The retort is then set on a wire gauze on a tripod stand, clamped in position and carefully heated by a Bunsen burner. The water boils, giving off steam which is condensed back to water in the receiver placed at the end of the stem of the retort ; this is pure water and is called the **distilled water.** The water collecting in the receiver is called the **distillate.** The dissolved solid and the muddy suspensions remain behind in the retort as a **residue.**

After a time the stem of the retort and the receiver get warm, and the condensation of steam is not efficient. Hence, when larger quantities of liquid are to be distilled it is convenient to use a **Liebig's condenser.**

The muddy water for distillation is taken in a flask (called a distilling flask) with a side tube fused on to the neck. The side tube is connected by means of a cork with the inner glass tube of a Liebig's condenser, itself surrounded by a wider jacket through which a constant stream of cold water is passed—the cooling water is passed in at the bottom, and out at the top of the condenser (fig. 19). The mouth of the flask is closed with a cork—a thermometer may be inserted in the vapour coming from the liquid. The flask is set up on a wire gauze on a tripod stand, clamped in position. On heating the flask, the liquid boils, and the vapour, while passing through the cold inner tube of the condenser, condenses back to the liquid state and collects in the receiver placed at the end of the condenser tube—the liquid collecting is the distillate, the dissolved solid left behind in the flask is the residue.

Distilled water is taken in a wash bottle (fig. 20) for common laboratory use.

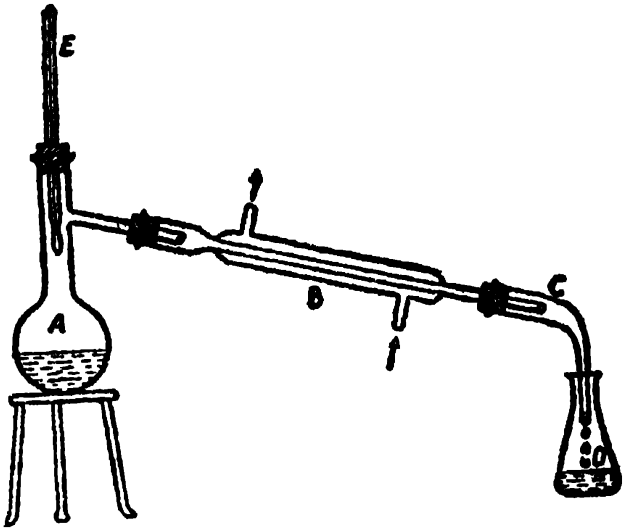


Fig. 19

When stirred with water potassium permanganate gives a pink solution. The coloured solution on distillation, produces a colourless distillate of pure water ; the potassium permanganate remains behind in the flask.

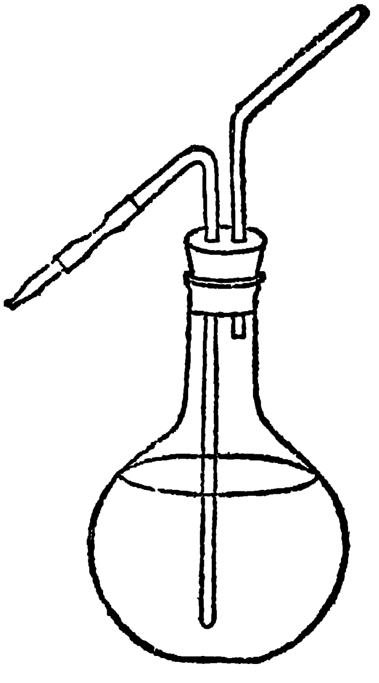


Fig. 20

Fractional distillation.—The process of distillation is useful to separate not only *solution of solids in liquids*, but also solutions of liquids in liquids, sometimes partially only.

When a solution of two volatile liquids with boiling points fairly apart, say, benzene and toluene with boiling points 80° and 110°C respectively, is heated in a distilling flask, each of the liquids gives off its vapour—the vapours formed will, however, contain a greater proportion of the *more volatile benzene* and a smaller proportion of the *less volatile toluene* than the original solution. The vapours on condensation give the distillate ; consequently the distillate is richer in benzene, and the liquid that remains behind in the flask is richer in toluene. This first distillate on second distillation, gives a second distillate which is still richer in benzene—the process may be repeated to finally yield a distillate which is pure benzene.

The residual liquid in the flask after the first distillation, when put to distillation again, leaves a residue still richer in toluene—repeated distillation of the residual liquid, therefore, yields pure toluene as the residue. By repeated distillation, therefore, benzene and toluene can be **completely** separated. To improve the separation, a **fractionating column** (fig. 21) is usually employed.

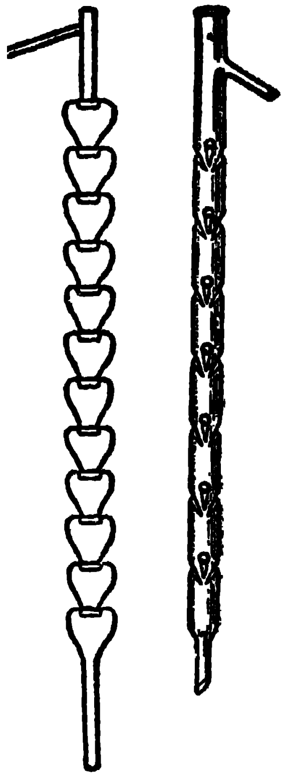


Fig. 21

The fractionating column is inserted between the distilling flask and the condenser.

Such a process of separation of volatile liquids by repeated distillation is known as fractional distillation.

Sometimes the separation is partial only ; thus when a *dilute* solution of hydrochloric acid is fractionally distilled, it is possible to separate pure water on the one hand, and a mixture of hydrochloric acid and water containing 20.2 per cent hydrochloric acid by weight, on the other.

A *dilute* solution of alchol on fractional distillation, yields pure water, and a mixture of alcohol and water containing 95.57 per cent alcohol by weight.

Vacuum Distillation.—The vapour pressure of a liquid increases or decreases as the temperature rises or falls. A liquid boils when its vapour pressure becomes equal to the superincumbent pressure of air on its surface. The boiling point of a liquid, therefore, rises or falls according as the super-incumbent pressure is increased or decreased. Hence when the pressure on the surface of a liquid is reduced by creating a partial vacuum inside the distilling flask, the liquid boils and distils at a temperature less than its normal boiling point—the extent of lowering depends upon the degree of vacuum created. The distillation unit for this purpose is connected through a manometer to a pump (fig. 22). Substances which decompose near about their boiling points at atmospheric pressure are usually distilled under reduced pressure. This is known as *distillation in vacuum.* Glycerine, for example, boils at 290°C with decomposition at atmospheric pressure, but when it is distilled under reduced pressure, its boiling point is reduced and the decomposition avoided ; glycerine, for example, distils undecomposed at 180° under under 12 mm. pressure. For a similar reason hydrogen peroxide is concentrated by distillation in vacuum. It may be safely distilled under reduced pressure—the boiling point at 68 mm. pressure is 84°, and at 26 mm. is 69° ; but it decomposes exclusively into water and oxygen at 151°, which is its boiling point at 760 mm. estimated byxa trapolation.

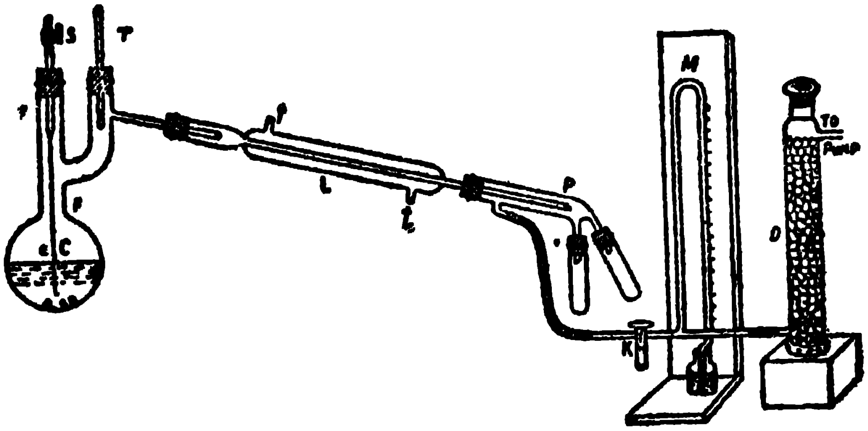


Fig. 22

Destructive distillation.—When coal is heated out of contact with the air in a closed vessel, it decomposes into several volatile and non-volatile products, thus a gas is given off, called coal gas, a tar is driven off, and an ammoniacal liquor collects ; the non-volatile products are the coke and the gas carbon.

Such a process of heating a substance like coal out of contact with the air, when it decomposes into volatile and non-volatile products, is known as destructive distillation, also called *dry distillation.*

The dry distillation of coal may be demonstrated in a very simple way. A hard glass test-tube is fitted with a cork and a delivery tube, as shown in the fig. 23—the end of the delivery tube leads into a test-tube which acts as a receiver. Some coal chips are put in the hard glass tube, and then heated fairly strongly : a brown coal tar collects below an aqueous liquor in the receiver test-tube ; a gas issues out through the exist tube, which may be burnt with a sooty flame. The solid residue left in the hard glass tube is the coke.

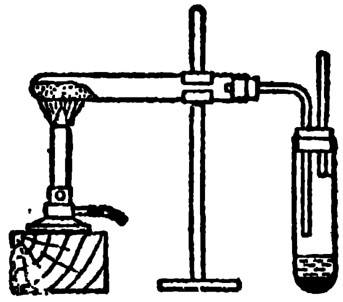


Fig. 23

Sublimation.—It is a common experience that most solids when heated long enough, first melt into a liquid which then vaporises. But there are certain volatile solids such as ammonium chloride, iodine, camphor, etc., which when heated pass *directly* into the vapour state without ever becoming a liquid—the vapour condensing into the *same* solid on cooling. The condensed solid is called the **sublimate** and the process **sublimation.** The sublimate has the same composition as the original substance. Thus when some ammonium chloride, also called *sal-ammoniac*, is heated in a dry test tube, the substance disappears from the bottom of the tube and reappears as a white deposit on the cool sides at the upper end of the tube ; ammonium chloride is said to sublime, and the white deposit is the sublimate. The peculiar thing to notice is that ammonium chloride *does not melt,* but turns into vapour without *ever becoming a liquid,* and the vapour condenses to the solid *directly.*

Sublimation is, therefore, *a process of vaporisation of* certain *solids without previous fusion.*

The process of sublimation is sometimes used in the purification of substances. Iodine, for example, is purified by sublimation. Volatile and non-volatile solids may be separated by sublimation.

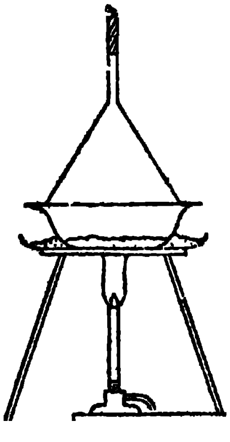
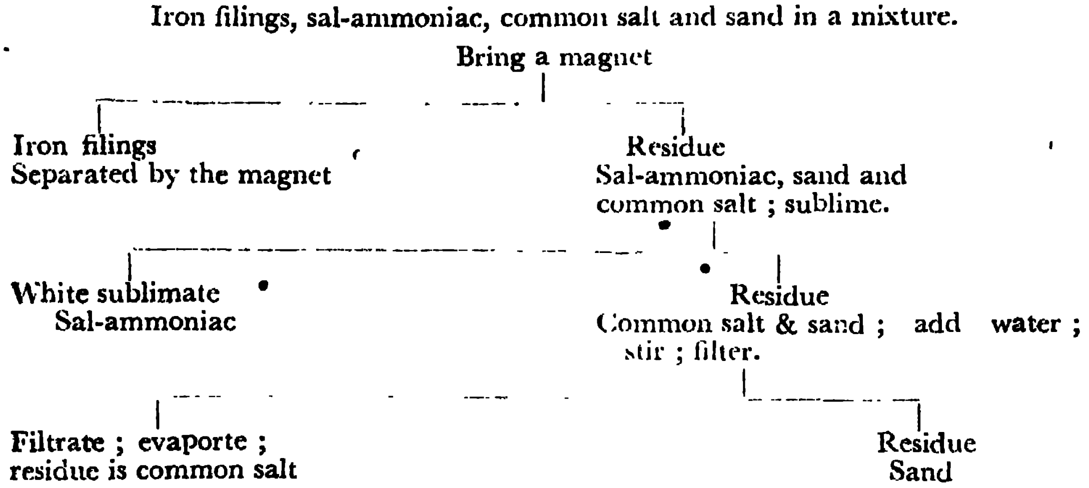


Fig. 24

To separate a mixture of ammonium chloride and sodium chloride.—Some of the mixture is put in a porcelain basin, and covered with an inverted funnel—the end of the stem of the funnel being closed with a paper plug. The basin is then slowly heated over a wire gauge (fig. 24). The ammonium chloride volatilises and collects as a white sublimate on the inner wall of the funnel. When no further sublimation occurs, the flame is removed and the sublimate of ammonium chloride is scraped off on to a filter paper. The nonvolatile sodium chloride remains behind in the basin.

To separate a mixture of sand, common salt, iron filings, and sal-ammoniac.—Some of the mixture is spread on a sheet of paper, and the iron filings are completely removed by brining a magnet several times over it—the iron filings alone are attracted by the magnet. The rest of the mixture, after the removal of iron filings, is put into a basin and covered with a funnel the stem of which is covered with a paper plug. On heating, the sal-ammoniac alone sublimes and deposits on the inner wall of the funnel. When no further sublimation occurs, the basin is allowed to cool; the funnel is removed and the sal-ammoniac scraped off. The residue of common salt and sand in the basin in shaken with sufficient quantity of warm water to completely dissolve out the salt, and filtered—the sand is the residue; this is dried and separated from the filter paper. The filtrate on evaporation gives the common salt.


Iron filings, sal-ammoniac, common salt and sand in a mixture.
Bring a magnet
Iron filings
Separated by the magnet
Residue
Sal-ammoniac, sand and common salt ; sublime.
White sublimate
Sal-ammoniac
Residue
Common salt & sand ; add water ; stir ; filter.
Filtrate ; evaporte ; residue is common salt
Residue
Sand

Crystallisation.—A cold saturated solution of copper sulphate is prepared by stirring the powdered salt with water, so that an excess of solid is present; the saturated solution is then warmed until all the solid remaining over has completely dissolved—a few drops of dilute sulphuric acid is added to the solution to prevent the decomposition of the sulphate. The hot solution is poured into a basin and then allowed to cool slowly, when it is found that a portion of the copper sulphate deposits by itself from the solution in the form of solids with a regular and definite geometrical shape; such deposited solids are called **crystals** and the process is known as **crystallisation.**

A **crystal** *is a homogeneous solid body bounded by perfectly plane faces, and having a regular and definite geometrical form, spontaneously assumed during its formation from a solution or from gaseous or liquid state. The geometrical form is an expression of the internal arrangement of the atoms.*

Most substances in the solid state are crystalline. A crystal of common salt is cubic, while alum forms octahedral crystals. Usually a piece of solid substance consists of a large number of small crystals which have stuck together.

Crystalline and amorphous solids.—Solids are classified as *crystalline* or *amorphous*. Many substances, such as alum, common salt, sulphur, and ice, separate in the form of crystals when deposited in the solid state from a solution or from a homogeneous melt. Crystals, as already stated, have a *characteristic geometrical form*—crystals are bounded by plane faces which cut one another at definite angles. The atoms are arranged in a definite order, constantly repeated, in a crystalline solid.

Amorphous solids, as their name implies, have no definite crystalline form. Pitch and glass are typical examples of amorphous solids.

When a pure crystalline solid is heated there is a sharp change from the solid to the liquid state at a definite temperature, called the *melting pont. A crystalline solid has a definite melting point.*

The melting point of a pure solid is remarkably constant—the melting point of ice, for example, is used to fit the zero of a Centigrade thermometer. When an amorphous solid is heated it does not melt sharply at a definite temperature, but it gradually softens, becomes mobile, and eventually acquires the properties of a liquid ; amorphous solids can, therefore, be regarded as super-cooled liquids.

When broken by a sudden blow, a crystal most easily breaks along certain planes ; a piece of mica splits up easily into thin sheets ; rock-salt breaks up easily into cubic or rectangular pieces. An amorphous solid, on the other hand, does not cleave along any particular plane when broken by a sharp blow, but fractures with equal ease in any direction.

The preparation of crystals.—Crystals may be prepared : (i) *by concentrating a dilute solution, usually by heat, and then cooling.* When a hot saturated solution of a substance, say potassium dichromate, is cooled slowly, the substance deposits in the form of orange-red crystals i.e., in the form of solids with regular and definite geometrical forms ; such deposits are called *crystals* and the process is known as *crystallisation.* In order to obtain crystals from a dilute solution the solution is taken in a basin and heated on a wire gauze until a drop of the liquid removed on the end of a glass rod begins to crystallise, indicating that the solution is saturated at a lower temperature. The substance then crystallises on cooling. Large crystals are not formed on rapid cooling. Slow and uniform cooling only gives large crystals.

Seeding with a crystal of the solid in question often breaks super-saturation and hastens crystallisation, depositing large crystals. Thus, in order to prepare a large crystal of alum, a perfect crystal of alum is suspended into a clear solution of alum by means of a thread from a glass rod. As the solution slowly evaporates the solid deposits on the suspended crystal, which gradually grows in size.

Evaporation of a solution at the ordinary temperature also yields crystals ; thus a solution of sulphur in carbon disulphide deposits pale yellow rhombic crystals (fig. 25) of sulphur, by the spontaneous evaporation of the volatile solvent.

(i) by *solidifying certain fused substances :* thus molten sulphur separates out in the form of needle-shaped crystals of monoclinic sulphur on solidification (fig. 26).

(ii) by *condensing the vapours of volatile solids :* thus iodine sublimes on heating, giving violet vapours, which condense to the solid directly yielding dark-grey, shining crystals of iodine.

Hydrates and anhydrous substances.—There are many salts which form crystals of definite composition *containing water ;* such crystals are called **hydrates.** The water of hydration is commonly known as **water of crystallisation.** When copper sulphate, for example, deposits in the solid state from its solution in water, it separates in the form of glistening blue crystals of blue vitriol, $CuSO_4,5H_2O$, which contains five molecules of water for every molecule of copper sulphate that separates. The water of crystallisation, therefore, forms an essential part of the composition of hydrates. Many salts, while crystallising from their aqueous solutions, separate in the form of hydrates, e.g., blue vitriol, $CuSO_4,5H_2O$; green vitriol, $FeSO_4,7H_2O$; potash alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$; washing soda, $Na_2CO_3,10H_2O$; Epsom salt, $MgSO_4$, $7H_2O$.

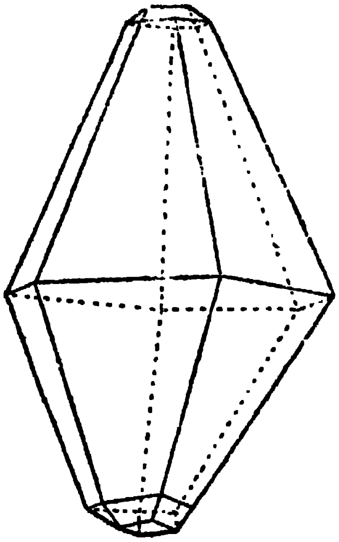


Fig. 25

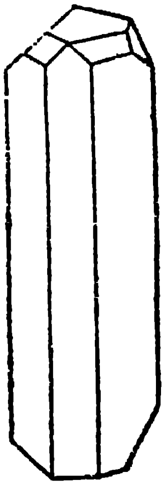


Fig. 26

The crystalline shape of the hydrates depends upon their water of crystallisation. A hydrate may often be made *anhydrous* by heating, when the water of crystallisation is driven off ; thus when some crystals of blue vitriol are heated in a test tube, steam is driven off, and the crystals fall to a white powder of *anhydrous* copper sulphate. When moistened, the white substance at once takes up water, and the blue copper sulphate is re-formed. The fact that anhydrous copper sulphate turns blue in presence of a trace of water is used as a delicate test for water.

The pink solution of cobalt chloride is sometimes used as '*invisible*' or '*sympathetic*' *ink*. Any writing done on a paper with weak cobalt chloride solution is practically invisible, but when the paper is held over a small flame the water of hydration of cobalt chloride is driven off, and the letters appear distinctly green or blue.

Water is not an essential part of all crystals. Common salt, NaCl, potassium nitrate, KNO_3, potassium chlorate, $KClO_3$, and ammonium chloride, NH_4Cl, are all anhydrous ; these salts crystallise without taking any water of crystallisation, and are, therefore, said to be **anhydrous.**

Fractional crystallisation.—Solids having different solubilities may often be separated from their mixed solutions and obtained in the pure state by a process, called fractional crystallisation. When such a solution is concentrated by heat, and allowed to cool slowly, it first gets saturated with the *least* soluble of the substances in solution, the excess of which, therefore, first deposits as crystals. Thus, when equal parts of common salt and potassium chlorate are dissolved in the minimum quantity of boiling water, and the solution allowed to cool it is found that the *less soluble potassium chlorate* separates first as crystals. These are filtered off, washed with a little water to dissolve out any adhering common salt, and dried. When not sufficiently pure, the crystals are often purified by re-crystallisation—the crystals are dissolved in a further quantity of boiling water and allowed to stand to cause *re-crystallisation.*

The filtrate, on concentration and cooling, gives crystals of common salt which are similarly filtered, re-crystallised, washed, and dried.

A further crop of crystals is often obtained on slight evaporation of the **mother liquor,** as the filtrate from the first deposit of crystals is commonly called.

The process of crystallisation is very often used in the laboratory to obtain a solid in the pure state—the process may have to be repeated several times before a pure crystalline solid is obtained ; a crystalline solid is characterised by a sharp melting point.

Madame Curie of radium-fame obtained a fraction of a gram of radium salt from a ton of pitch blende by this process of fractional crystallisation.

Determination of water of crystallisation.—The percentage of water of crystallisation in a given sample of a hydrate, say **barium chloride crystals,** $BaCl_2,2H_2O$, may be found out in the following way :

A porcelain crucible together with its lid, is carefully cleaned and dried. It is then heated on a clay-pipe triangle with a Bunsen flame (fig. 7), and allowed to cool in a desiccator. The crucible with its lid is then weighed in a chemical balance. About 1 gm. of barium chloride is then put into the crucible and weighed again. The crucible is then heated on the triangle, first gently and then strongly for about 20 minutes, with the lid kept partially open for the steam to be driven off. After the heating the crucible is allowed to cool in the desiccator, and the crucible with its lid and the contents is weighed again. The crucible is again heated for about 10 minutes, cooled and weighed again. This weight should be the same as before ; if not, the process is repeated till the weight is constant. The results are entered in a table as follows :

Weight of crucible + lid	a gm.
Weight of crucible + lid + barium chloride crystals	b gm.
Weight of crucible + lid + anhydrous barium chloride	c gm.
Weight of barium chloride crystals	(b−a) gm.
Weight of water of crystallisation	(b−c) gm.
Weight of anhydrous barium chloride	(c−a) gm.

$\therefore$ percentage of water of crystallisation $= 100 \times (b-c)/(b-a)$

Formula of barium chloride crystals.—Let the formula be $BaCl_2,nH_2O$, i.e., anhydrous $BaCl_2 : H_2O = 1 : n$. Therefore, as per above analysis :

$$\frac{\text{weight of anhydrous } BaCl_2}{\text{weight of water of crystallisation}} = \frac{1 \times \text{mol. wt. of } BaCl_2}{n \times \text{mol. wt. of } H_2O}$$

$$\text{i.e., } \frac{(c-a)}{(b-c)} = \frac{208.3}{18n} \text{ [mol. wt. of } BaCl_2 = 208.3].$$

The water of crystallisation in barium chloride crystals is 14.73 per cent.

$$\frac{100-14.73}{14.73} = \frac{208.3}{18n} \quad n = 2 \quad \therefore \text{ the formula is } BaCl_2, 2H_2O.$$

The water of crystallization of copper sulphate crystals.—It is usually determined by carefully heating the crystals on a watch glass in an air oven (fig. 27), because the copper sulphate itself is decomposed in strong heating over a direct flame.

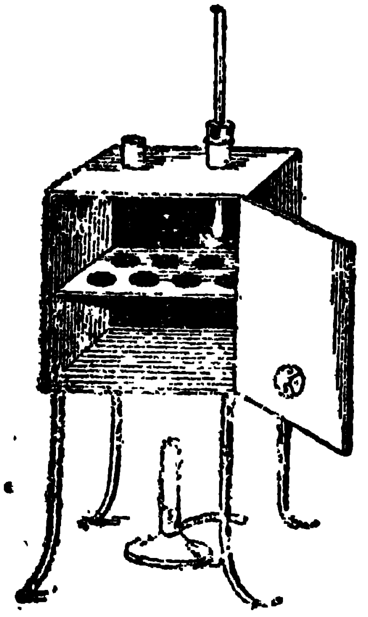


Fig. 27

About 1 gm. of powdered copper sulphate crystals is put into a watch glass provided with a cover watch glass and a clip—the pair of watch glasses together with the clip being weighed previously, and weighed again. The watch glass with its content of copper sulphate crystals is then heated in air oven to nearly 250°C for about 15 minutes, with the upper watch glass and the clip being taken out—the water of crystallisation is driven off as steam. The watch glass with its content of anhydrous copper sulphate is then cooled in a desiccator and weighed together with the upper watch glass and the clip. The watch glass is again heated for about 5 minutes, and cooled and weighed again as before. The weight should be the same as before, if not, the process of heating, cooling and weighing is continued till the weight is constant.

The results are entered in table as follows

	Weight of watch glasses + clip	a gm.
	Weight of watch glasses + clip + copper sulphate crystals	b gm.
	Weight of watch glasses + clip + anhydrous copper sulphate	c gm.
∴	Weight of copper sulphate crystals	(b −a) gm.
	Weight of water of crystallisation	(b −c) gm.
	Weight of anhydrous copper sulphate	(c—a) gm.

∴ percentage of water of cristallisation $= 100 \times (b-c)/(b-a) = 36{\cdot}07$

Formula of blue vitriol.—Let the formula be $CuSO_4, nH_2O$, i.e., the rati of anhydrous $CuSO_4$ to $H_2O = 1 : n$. Therefore, as per above analysis :

$$\frac{\text{weight of anhydrous } CuSO_4}{\text{wt. of water of crystallisation}} = \frac{1 \times \text{mol. wt. of } CuSO_4}{n \times \text{mol. wt. of } H_2O}$$

$$\text{i.e., } \frac{(c-a)}{(b-c)} = \frac{159.5}{18n} \text{ [mol. wt. of } CuSO_4 \text{ is 159.5]}$$

$$\therefore \quad \frac{100-36.07}{36.07} = \frac{159.5}{18n} \quad \therefore \ n = 5 \quad \therefore \text{ blue vitriol is } CuSO_4,5H_2O.$$

Efflorescence.—The stability of a hydrate depends on the pressure of water vapour in the atmosphere with which it is in contact. Every hydrate exhibits a definite vapour pressure at the temperature of the room ; when this pressure is greater than the pressure of the water vapour in air, the hydrate in question loses its water of crystallisation, and falls to a powder. Thus, the clear transparent crystals of washing soda, when exposed to the air, become opaque and white and crumble to powder. There is also loss in weight. The change is due to the loss of water from the crystals—washing soda, $Na_2CO_3,10H_2O$, losses 9 molecules of its water of crystallisation and become coated with an opaque layer of the monohydrate Na_2CO_3,H_2O. The washing soda is an efflorescent substance, and the phenomenon is called **efflorescence.**

Efflorescence *is a phenomenon in which a hydrate crumbles to powder, when exposed to the air, due to the loss of all or part of its water of crystallisation.*

Deliquescence.—The vapour pressure of a solution is less than that of pure water—the more concentrated the solution is, the less is its vapour pressure. The vapour pressure of very soluble substances, such as calcium chloride and caustic soda, for example, is very small indeed. It may be even less than the vapour pressure of water vapour in the air : in such a case, the solids, when exposed to the air absorb moisture from the atmosphere and gradually dissolve in it. They are known as deliquescent substances. Thus, when some calcium chloride is put on a watch-glass on the bench, it quickly draws moisture from the air, becomes sticky and finally dissolves. It is a good example of a deliquescent substance. Magnesium chloride, calcium chloride, and caustic soda, etc., are all deliquescent.

Deliquescence *is a phenomena in which a solid, when exposed to the atmosphere, dissolves in the moisture it absorbs from the air.*

It is worth remembering that pure common salt is not a deliquescent substance. The impure common salt contains small quantities of calcium and magnesium chlorides, and as such it becomes damp or deliquesces, when exposed to the air.

Some substances such as quick lime, glass, porcelain, black copper oxide, and anhydrous copper sulphate, aborb moisture on exposure to the damp air but do not dissolve in it : these are called hygroscopic substances. Deliquescent and **hygroscopic** substances are consequently kept in closed bottles.

Desiccation.—It is a process of drying, i.e., removing moisture from substances. Deliquescent substances like fused calcium chloride, fused zinc chloride, solid caustic potash, and phosphorus pentoxide, etc., are the usual drying agents. Quick lime and concentrated sulphuric acid are also commonly employed. Silica gel is often used to remove moisture from substances.

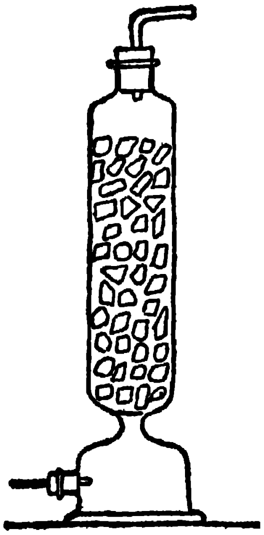


Fig. 28

The *desiccating* agents should be capable of absorbing moisture only but having no chemical action on the substances to be dried.

Gases are usually dried by passing through such drying agents as quick lime, phosphorus pentoxide and fused calcium chloride, etc., contained in *drying towers* (fig. 28) or *U-tubes* or by sending a stream of gas through *wash bottles* (fig. 29) containing sulphuric acid or a drying tower packed with pieces of pumice soaked in the acid. *liquids* are best dried by keeping them in contact with a suitable solid drying agent, which is subsequently removed by filtration. *Solids* are dried, according to their nature, in one of the following ways :

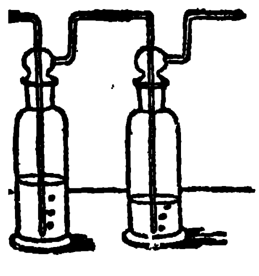


Fig. 29

(a) **At the room temperature** for substances to unstable to be dried by heating. Such substances are dried in a *desiccator* (fig. 31) which is an air-tight thick-walled glass vessel provided with a lid which fits accurately and perfectly air-tight on the upper ground rim of the desiccator, which is greased. The desiccator is contracted at the middle—a circular perforated zinc-sheet placed on a shelf above the constriction, separates the upper from the lower half. The air inside the desiccator is kept dry by putting such drying agents as fused calcium chloride or concentrated sulphuric acid at the bottom. The substance to be dried is kept on a clay-pipe triangle in the upper half. A *vacuum desiccator* (fig. 30) is often used for quick drying. A desiccator not only *dries* a substance but also *prevents it from coming in contact with atmospheric moisture.* Hence hygroscopic substances are kept inside desiccators after they have been dried by heat.

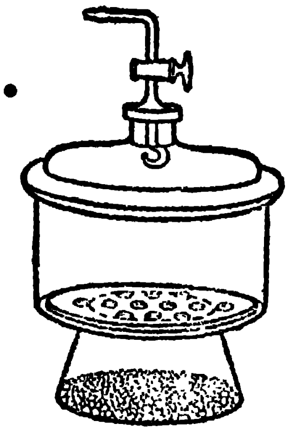


Fig. 30

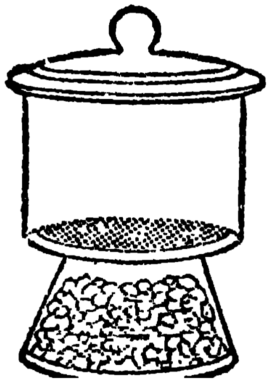


Fig. 31

(ii) **At steam heat.**—Steam oven (fig. 32) is used for drying up to 100°C. It is a double-walled copper vessel with a hinged door and a movable perforated shelf inside. The hollow space between the two walls is partially filled with water through an opening at the top—the water is kept boiling by heating the oven with a gas-burner from below, when the upper portion of the hollow casing is filled with steam. The substance to be dried is put on the shelf inside the oven where the temperature is nearly 100°C.

(iii) **Above steam-heat**—*Air-oven* (fig. 27) is used for drying above 100°C. It is a copper vessel with a hinged door and a movable perforated shelf. The desired temperature is obtained by regulating the gas-burner with which the oven is heated. A thermometer inserted through a cork on the top of the oven records the temperature.

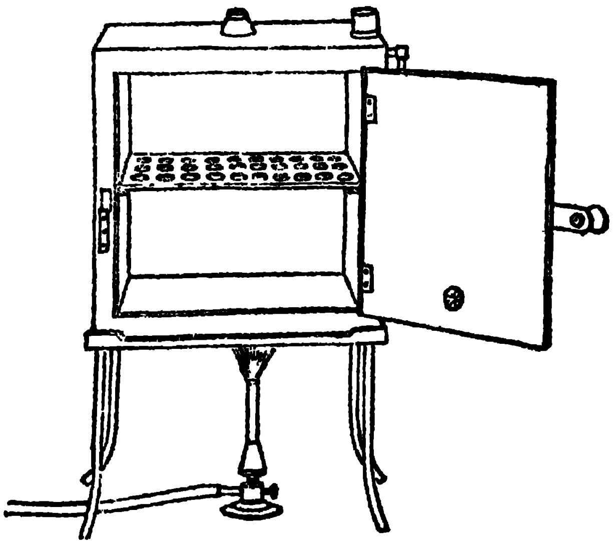


Fig. 32

Selection of drying agents depends on the nature of the substances to be dried. Drying agents should only absorb the moisture but must not react with the substance to be dried. Basic substances are, therefore, usually, but not always, dried by basic substances ; and the acidic substances usually by the acidic drying agents. An acidic oxide such as carbon dioxide, for example is dried by strong sulphuric acid or phosphorous pentoxide which are themselves acidic or by fused calcium chloride which does not absorb the gas. Sulphuretted hydrogen is acidic ; it is either dried by calcium chloride or phosphorous pentoxide, but not by sulphuric acid, since the latter reacts with sulphuretted hydrogen. Ammonia is basic and is best dried by quick lime which is also basic. It is not dried by means of calcium chloride since it absorbs the gas. Neutral gases like oxygen, nitrogen, carbon monoxide, nitrous oxide, etc., may be dried by any of calcium chloride, sulphuric acid, phosphorus pentoxide, etc.

Separation of ingredients of a mixture.—(*i*) **Solids in a mixture.**—Separation may be effected in different ways, e.g.,

(a) *By solution.*—When a mixture of sand and sulphur, for example, is shaken with sufficient carbon disulphide, sulphur dissolves. The solution is filtered—the filtrate on evaporation gives crystals of sulphur. The residue on the filter paper is sand.

(b) *By sublimation.*—When a mixture of quick lime and iodine is heated, iodine forms violet vapours which may be condensed to a deep violet shining sublimate ; lime being non-volatile is left behind.

(c) *By difference in density.*—Tin stone (a mineral of tin) is separated from earthy impurities by washing with a stream of water which carries away the lighter earthy matter (specific gravity 2.7), while the heavier tinstone (sp. gr. 7) is left behind.

(d) *By floatation.*—When air is sent through a suspension of finely pulverised sand and zinc blende (a mineral of zinc) in water to which a little oil is added, a froth forms. This catches the zinc blende which floats, while the sand is wetted by water and sinks to the bottom.

(e) *By magnetic attraction.*—A magnet separates a magnetic substance from its mixture with non-magnetic substances. Iron filings, for example, may be thus separated from sand.

(f) *By fusion.*—When a mixture of sand and lead is heated, the latter melts to a liquid upon which sand floats. Easily fusible solids like sulphur (m.p. 114°C), tin (m.p. 232°C), etc., may be separated from rocky impurities by this means.

(ii) **Solids and liquids in a mixture.**—Separation may be effected by : (a) *Sedimentation* and *filtration.* Coarse suspensions deposit on standing, the clear liquid from the top may then be decanted off carefully ; the liquid is, however, filtered from the insoluble solids for complete separation : (b) *Distillation* : Non-volatile solids in solution or suspension are separated by distillation.

(iii) **Liquids in a mixture.**—Separation is usually effected : (a) by *fractional distillation,* (b) by means of a separating funnel when the liquids are immiscible and form separate layers, such as mixture of ether and water.

(iv) **Gases in a mixture.**—Separation may be effected by : (a) *liquefaction.*—When a mixture of hydrogen and carbon dioxide, for example, is cooled and compressed to a few atmospheres only, carbon dioxide alone liquefies and may be easily removed. When a mixture of sulphur dioxide and oxygen is cooled in a freezing mixture of ice and common salt, the sulphur dioxide alone liquefies.

(*b*) *Different solubilities in liquids.*—Traces of hydrochloric acd, for example, is removed from its mixture with chlorine by passing the mixed gases through water in which the hydrochloric acid is much more soluble than chlorine.

(*c*) *Chemical absorbents.*—Absorbents which selectively react with certain gases, forming non-volatile products. Acidic gases such as carbon dioxide and sulphur dioxide, for example, are separated from their mixture with neutral gases like hydrogen, oxygen, carbon monoxide, etc., by washing with a solution of caustic potash.

The gases may also be separated by *diffusion.*

Extraction with a liquid.—A solution is sometimes extracted with another liquid which preferentially dissolves the solute. When an aqueous solution of hydrogen peroxide, for example, is shaken with ether in a separating funnel, the hydrogen peroxide dissolves mostly in the ether. Two distinct layers are formed—the top ether layer contains most of the hydrogen peroxide ; this is separated and taken into a basin. On keeping for sometime the ether which is highly volatile evaporates by itself, and the hydrogen peroxide remains behind as a colourless liquid.

Lixiviation.—Lixiviation refers to extraction, i.e., dissolution of the soluble component of a solid mixture by means of a suitable solvent ; the term is usually used for large scale extraction only, e.g., lixiviation of *kelp or black ash* with water. The term **leaching** also refers to extraction with a solvent.

Types of chemical reactions.—Different types of chemical changes are usually distinguished thus—(i) **Synthesis.**—It is a process in which a compound is formed by direct union of its constituents. Heated sodium burns in chlorine forming sodium chloride. When heated in air, mercury forms mercuric oxide. Water is produced when hydrogen and oxygen are sparked together. Ammonia combines with hydrochloric acid giving ammonium chloride. Carbon dioxide combines with heated quick lime forming calcium carbonate.

$$2Na + Cl_2 = 2NaCl \; ; \; 2Hg + O_2 = 2HgO.$$

$$2H_2 + O_2 = 2H_2O \; ; \; NH_3 + HCl = NH_4Cl.$$

$$CaO + CO_2 = CaCO_3.$$

(ii) **Analysis** (also called decomposition).—It is a process in whcih a compound breaks up into two or more simpler substances. It is thus reverse of synthesis. When strongly heated mercuric oxide decomposes into mercury and oxygen. Acidulated water decomposes into hydrogen and oxygen on electrolysis. Chalk breaks up into calcium oxide and carbon dioxide on heating. Potassium chlorate yields potassium chloride and oxygen on heating.

$$2HgO = 2Hg + O_2 : CaCO_3 = CaO + CO_2$$

$$2KClO_3 \text{ (potassium chlorate)} = 2KCl \text{ (potassium chloride)} + 3O_2$$

(iii) **Displacement.**—It is a process in which one element displaces another from a compound and takes its place. A clean piece of iron dipped in copper sulphate solution gets coated with a red deposit of copper, while iron goes into solution as ferrous sulphate. Zinc displaces hydrogen from sulphuric acid, forming zinc sulphate.

$$Fe + CuSO_4 \text{ (copper sulphate)} = Cu + FeSO_4 \text{ (ferrous sulphate).}$$

$$Zn + H_2SO_4 \text{ (sulphuric acid)} = H_2 + ZnSO_4 \text{ (zinc sulphate).}$$

(iv) **Isomerism.**—A compound is said to undergo an isomeric change when it changes by internal rearrangement of its atoms into another substance with different properties but *having the same percentage composition*. Ammonium cyanate changes into urea on heating. Ammonium cyanate and urea are said to be *isomers*.

$$NH_4CNO \text{ (ammonium cyanate)} = H_2N-CO-NH_2 \text{ (urea).}$$

(v) **Double decomposition** or **metathesis.**—It is a process in which two compounds, usually acids, bases and salts, react chemically so as to exchange their constituent parts or radicals, producing two new compounds. When a solution of common salt is added to silver nitrate solution, they react chemically, producing a curdy white precipitate of silver chloride, and sodium nitrate which remains in solution :

$$NaCl + AgNO_3 = AgCl + NaNO_3$$

Calcium chloride solution reacts with a solution of sodium carbonate, giving sodium chloride and a white precipitate of calcium carbonate :

$$CaCl_2 + Na_2CO_3 = 2NaCl + CaCO_3$$

Precipitation.—When solutions of two substances are mixed together, an insoluble solid sometimes separate by double decomposition—the solid separating is called the precipitate and the process is known as precipitation. A heavy white precipitate of barium sulphate is produced by mixing together solutions of barium chloride and sulphuric acid :

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$$

A black precipitate of copper sulphide is produced by passing a stream of hydrogen sulphide gas into copper sulphate colution :

$$CuSO_4 + H_2S = CuS + H_2SO_4$$

When hydrogen chloride (HCl gas) is passed into a saturated solution of common salt, pure sodium chloride, NaCl, precipitates out in the form of colourless transparent crystals.

(iv) **Hydrolysis.**—A compound is said to undergo hydrolysis when it is split up by water, either completely or partially, producing new substances.

$$PCl_3 + 3H_2O = H_3PO_3 \text{ (phosphorous acid)} + 3HCl$$

$$Na_2CO_3 + H_2O \rightleftharpoons NaHCO_3 \text{ (sodium bicarbonate)} + NaOH$$

There are many other types of reactions such as dissoication, disproportionation, neutralisation, oxidation, reduction, catalytic reaction, etc.

Modes of bringing about chemical action.—Chemical changes are brought about by one or more of the following means :

(i) **Contact.**—Yellow phosphorus takes fire in contact with iodine. Few crystals of iodine and small pieces of yellow phosphorus are placed in different parts of a basin—on bringing them in contact phosphorus catches fire.

$$P + 3I = PI_3$$

(ii) **Solution.**—Substances are brought into closer contact in solution and hence react readily. *Baking powder* contains tartaric acid and sodium bicarbonate which do not react when dry ; on adding water a brisk reaction occurs with evolution of carbon dioxide.

(iii) **Heat.**—Heating expedites most chemical changes, but there are reactions which occur only on the application of heat. Decomposition of hydrogen peroxide into water and oxygen is accelerated by heat. Mercuric oxide, potassium chlorate, etc., decompose only when heated.

$$2H_2O_2 = 2H_2O + O_2 \; ; \quad 2HgO = 2Hg + O_2$$

(iv) **Light.**—Certain reactions occur only in presence of light. When exposed to sunlight a mixture of hydrogen and chlorine explodes violently to form hydrogen chloride, but no action takes place in the dark. $H_2 + Cl_2 = 2HCl$.

Silver salts are affected by sunlight and so also the photographic films which contain silver halides.

Sound.—When mercury fulminate is exploded near acetylene, C_2H_2, the latter is decomposed into carbon and hydrogen.

(vi) **Pressure** or **percussion.**—Chemical action may sometimes be induced under the influence of pressure. Finely powdered lead and sulphur may be made to combine together under high pressure, forming lead sulphide : $Pb + S = PbS$. *Crackers* which usually contain a mixture of arsenic sulphide and potassium chlorate, explode with a loud report on percussion. Gunpowder also explodes on percussion.

(vii) **Electricity.**—Many chemical changes are brought about by electricity. Acidulated water separates into hydrogen and oxygen on electrolysis. Nitric oxide is formed from its elements under the influence of electric sparks.

$$N_2 + O_2 = 2NO$$

(viii) **Catalyst.**—Many chemical reactions are influenced by catalysts. Decomposition of hydrogen peroxide into water and oxygen is greatly increased in presence of finely-divided platinum which acts as a catalyst.

$$2H_2O_2 = 2H_2O + O_2$$

Solution of gases in liquids.—Gases are only partially miscible with liquids. Carbon dioxide is fairly soluble in water. Air is only slightly soluble in water—dissolved air supports the life of aquatic animals. The amount of gas that would dissolve in a given quantity of water depends on : (i) the nature of the gas, (ii) the temperature and (iii) the pressure of the gas in contact with water.

The neutral gases, e.g., hydrogen, oxygen, nitrogen, etc, are only slightly soluble in water ; the acid (e.g., hydrogen chloride, sulphur dioxide) or alkaline gases (e.g., ammonia) are highly soluble in water, as they react chemically with it. Unlike solids, the solubility of a gas in liquids decrease with rise in temperature. The solubility of a gas, however, increases with pressure.

Henry's law.—The effect of pressure on the solubility of gas in liquids is given by Henry's law which states : *"the amount of gas dissolved by a given volume of liquid at constant temperature is proportional to the pressure."*

If w is the mass of gas dissolved by unit volume of liquid, i.e., concentration of gas in solution, at a pressure p, then

$$w \propto p, \text{ or } w = sp, \text{ i.e., } w/p = s,$$

where s is a constant ; also *concentration of gas in solution* $= s \times$ *pressure.* But since pressure is a measure of the concentration of the gas in the space above the liquid, Henry's law is also stated thus : at a given temperature

$$\frac{\text{concentration of gas in solution}}{\text{concentration of gas in gas phase}} = \text{constant} = s.$$

s is called *solubility coefficient* of the gas in the liquid for the given temperature, and may be defined as the volume of gas dissolved by 1 c.c. of the liquid at the temperature of the experiment. If v be the volume of gas absorbed by V c.c. of liquid at t° then solubility co-efficient $s = v/V$.

Reduced to N.T.P. s becomes equal to $273 \times s/(273 + t)$.

This is referred to as *absorption coefficient of the gas* which may be defined as the volume of gas, *reduced to N.T.P.*, that is dissolved by 1 c.c. liquid at a given temperature and and under a pressure of 1 atmosphere ; solubility of a gas is often expressed by its absorption co-efficient S which is related to s by the expression :

$$S = 273 \times s/(273+t).$$

The solubility may also be expressed as weight of gas dissolved by 1 c.c. of liquid.

Henry's law is very nearly true for sparingly soluble gases. For carbon dioxide, the law holds at small pressures, but wide variations are found at high pressures.

The law does not apply to very soluble gases, such as ammonia at ordinary temperature or hydrogen chloride, in water. At 100°C when ammonia is much less soluble Henry's law is nearly true.

Solubility of mixture of gases.—According to Dalton's law of partial pressures, the partial pressure of a gas is unaffected by the presence of other gases, hence its solubility would also be unaffected. Therefore, *in a mixture of gases, the solubility of each gas is proportional to its partial pressure.*

Exercise.—The absorption co-efficients of nitrogen, oxygen and argon at 0°C, and the composition by volume of these gases in dry carbon dioxide-free air, are given. Find the percentage composition by volume of the gas expelled by boiling from water saturated with air at 0°C. The partial pressures of these gases in air at 1 atmosphere are proportional to the volume percentages.

Gas	Percentage by volume.	Partial pressure in atmosphere	Absorption co-efficient
Nitrogen	78	0.78	0.0239
Oxygen	21	0.21	0.0489
Argon	1	0.01	0.0530

These gases dissolve in water in amounts proportional to their absorption co-efficients and to their partial pressures.

Therefore, 1 litre of water dissolves from air at 0°C and 1 atmosphere.

Nitrogen	...	$1{,}000 \times 0.0239 \times 0.78$	$= 18.65$ c.c.	$= 63.3\%$
Oxygen	...	$1{,}000 \times 0.0489 \times 0.21$	$= 10.27$ c.c.	$= 34.9\%$
Argon	...	$1{,}000 \times 0.053 \times 0.01$	$= 0.53$ c.c.	$= 1.8\%$

Total volume of gas dissolved $= 18.65 + 10.27 + 0.53 = 29.45$ c.c.

$\therefore \ \%N_2 = 18.65 \times 100/29.45 = 63.3$; $\%O_2 = 10.27 \times 100/29.45 = 34.9$, etc.

When the dissolved gas is expelled by boiling, its percentage composition by volume is 63.3% N_2, 34.9% O_2 and 1.8% A. It is richer in oxygen and argon than original air, since they have higher absorption co-efficients than nitrogen.

Exercises

1. What do you understand by the terms *solution* and *solubility* ?

Describe fully how you would determine the solubility of potassium nitrate at the temperature of the room. Why is it necessary to specify the temperature while referring to the solubility of a substance ?

2. Explain the terms *saturated solution* and *super-saturated solution.* How does a solution differ from a compound ?

One hundred grams of water dissolve the following weights of ammonium chloride at the temperature named :

Temperature	0°	10°	20°	30°	40°	50°	60°	80°	100°	
Substance	28.4	32.8	37.3	41.4	46.2	50.6	55.0	64.0	72.8	gram.

Construct the solubility curve of the substance, and from the curve determine the solubility of ammonium chloride at 24° and 70°.

What information can be obtained from the study of solubility curves ?

3. What is meant by (*i*) crystal, (*ii*) *crystallisation* ?

Explain how you would grow a large crystal of alum. Has the rate of cooling any effect on the size of crystals deposited ?

You are given a mixture of common salt and potassium nitrate. How would you obtain pure specimens of both the materials from the solution ?

4. What is meant by water of crystallisation ? Describe how you would determine the percentage of water of crystallisation in copper sulphate crystals. Copper sulphate crystals contain 36.07 per cent of water of crystallisation ; 5 grams of copper sulphate crystals are heated. Calculate the loss of weight. *Ans.* 1.8

5. Explain the terms (i) *efflorescence* and *deliquescence*, (ii) *hydroxide* and *hydrate.* Illustrate your answer with suitable examples.

How would you find out if washing soda is efflorescent or deliquescent ?

6. Explain fully what is meant by (a) *distillation*, (b) *sublimation*.

How would you separate a mixture of ammonium chloride and common salt ?

A sample of muddy water is provided. How would you find if the water contained any dissolved salt in it, and how would you obtain a sample of pure water from it ?

7. Describe how you would separate the ingredients in each of the following. noting the properties of the ingredients which help you in separating them :

(i) a mixture of common salt and nitre,
(ii) a mixture of silver chloride and lead chloride,
(iii) a mixture of iron filings and sulphur,
(iv) a mixture of sand and chalk.
(v) a mixture of sand and lead shavings.

8. How would you separate :

(i) a mixture of sand, chalk, and common salt,
(ii) a mixture of bromine, sodium sulphate and sand,

(iii) a mixture of iodine, common salt, and powdered glass.
(iv) a mixture of hydrogen and carbon dioxide,
(v) a mixture of alcohol and water,
(iv) gunpowder into its constituents ?

How would you prove that the gunpowder is a mixture ?

9. Explain the terms *analysis* and *synthesis*. Illustrate your answer with examples How would you separate water into its constituents ?

10. Explain the meaning of the terms : (a) solution, (b) sublimation, (c) solubility, (d) solubility curves. How are solubility curves drawn and what is their use ?

11. State briefly the principal modes and conditions of chemical action. Give examples of each.

12. The residue from 1 gm. of crystallised barium chloride after it had been heated till no further loss of weight occured, weighed 0.853 gm. What is the formula of the crystallised salt ? *Ans.* $BaCl_2,2H_2O$

13. Blue vitriol is represented by the formla $CuSO_4.nH_2O$; 1 gm. of the sample on being heated, was reduced to a constant weight equal to 0.64 gm. Find the value of n. *Ans.* 5

14. Write notes on Henry's law of solubility of gases in liquids.

VI

PHYSICAL PROPERTIES OF GASES

The laws governing the behaviour of gases under different conditions of temperature and pressure are, to a large extent, independent of the nature of the gas. Boyle's law (1662) states the effect of pressure on the volume of a gas. The law of variation of volume of gas with temperature was stated by Gay Lussac in 1802 but often called Charles's law, since similar results were obtained by Charles in 1787, although they were not published at that time.

Boyle's Law.—*At constant temperature, the volume of a given mass of any gas is inversely proportional to the pressure.* In other words, if pressure is brought to bear upon a known volume of a gas, this volume will decrease as the pressure increases, and *vice-versa.*

If the pressure on a gas, for example, is doubled, its volume will be reduced to one-half of what it was originally. Mathematically, the Boyle's law may be stated in the form : temperature remaining constant, $v \propto 1/p$, or $pv = k$,
where p is the pressure and v the volume of the given mass of gas, and k is a constant.

If p_1 and v_1 are the pressure and volume of a given mass of a gas, and p_2 and v_2 are the pressure and volume of the same amount of the gas consequent to some change in initial pressure or volume, then

$$p_1v_1 = k \text{ and } p_2v_2 = k, \text{ so that } p_1v_1 = p_2v_2$$

Boyle's law is also known as Marriotte's law.

Charles's law.—*At constant pressure, the volume of a given mass of any gas expands by* 1/273 of its volume at 0°C *for each* 1°C *rise in temperature.*

Stated in the symbols,

$$v_1 = v + v.\frac{t_1}{273} = v\left(1 + \frac{t_1}{273}\right) = v\left(\frac{273 + t_1}{273}\right)$$

where v is the initial volume of the gas at 0°C and v_1 is the volume after the temperature has been raised to t_1°C.

It is found that when $t_1 = -273°C$, the volume becomes zero, that is, if a gas were cooled to −273°C, it would have occupied no volume at that temperature, which is called the **absolute temperature.** The absolute temperature is obtained by taking −273°C as zero degree absolute. This is denoted by T.

Thus, 0°C = 273° absolute ; t°C = (t+273)° absolute.

Let v_1 and v_2 be the volumes of a given mass of a gas at temperatures t_1°C and t_2°C respectively ; then :

$$v_1 = v\left(\frac{273 + t_1}{273}\right) \text{ and } v_2 = v\left(\frac{273 + t_2}{273}\right)$$

$$\therefore \frac{v_1}{v_2} = \frac{273 + t_1}{273 + t_2} = \frac{T_1}{T_2}, \text{ i. e., } \frac{v}{T} = \text{constant.}$$

Consequently, $v \propto T$, when pressure remains constant.

The volume of a given mass of any gas at constant pressure, therefore, *is directly proportional to its absolute temperature.* This is an alternative expression for Charles's law.

Equation of state.—The results of Boyle's law and Charles's law may be combined in an expression giving a relation between temperature, pressure and volume of a given mass of a gas—such an equation is known as an equation of state.

Since for a given mass of a gas :

(i) $v \propto 1/p$, when T remains constant (Boyle's law) ;
(ii) $v \propto T$, when p remains constant (Charles's law) ;
$\therefore$ $v \propto T/p$, when both T and p vary.

$$\therefore v = k\frac{T}{p}, \text{ where k is a constant, i.e., } \frac{pv}{T} = \text{constant}$$

for given mass of a gas.

This equation of state, pv/T = constant, implies that for a given mass of gas, any change of temperature and pressure would cause a corresponding change in volume, so that the quantity pv/T remains constant.

If p_1, v_1, T_1 and p_2, v_2, T_2 are the pressure, volume and temperature of a given mass of a gas under two sets of conditions then

$$\frac{p_1v_1}{T_1} = \frac{p_2v_2}{T_2}$$

This equation enables us to find out the volume of a given mass of gas if its temperature and pressure are changed.

For any conditions of temperature and pressure pv/T = constant. When the mass of gas taken is 1 gram molecule, the constant, then known as the **molar gas constant**, is written as R. Hence the ideal gas law equation for 1 mole is pV = RT.

where V is the volume of 1 gram molecule of the gas, i.e., the molar volume, at the pressure p and the temperature T. Value of R may be found out from the fact that one gram molecule of a gas occupies 22.4 litres at 0°C and 1 atmosphere pressure. Then $T = 273°$ absolute, $p = 1$ atmosphere, $V = 22.4$ litres.

$\therefore$ $R = 1 \times 22.4/273 = 0.082$ litre-atmosphere per degree absolute per gram molecule.

For n gram molecules of a gas, at the same temperature and pressure, the volume would be n times as great as for 1 mole ; let this volume be v, then the above equation becomes : $pv = nRT$. $p \times \frac{v}{n} = RT$

Now, $n = w/M$, where w = mass of gas, and M = molecular weight of the gas.
$\therefore$ $pv = nRT = wRT/M$; $\therefore$ $M = wRT/pv$.

Again, mass per unit volume, w/v = density of gas, d,

$$\therefore \quad M = \frac{wRT}{pv} = \frac{d}{p} RT.$$

From the above relations molecular weight of a gas can be calculated.

Density of a gas.—Density of a gas is the mass per unit volume.

Stated in symbols, $d = w/v$, or $w = v \times d$,

where w is the mass, v the volume and d the density of gas.

At constant temperature the density of a given mass of gas is inversely proportional to its volume, i.e., if the volume increases, the density will correspondingly decrease, i.e., $d \propto 1/v$.

Now, at constant temperature $v \propto 1/p$; *hence at constant temperature density of given mass of gas is directly proportional to pressure,*

i.e., T remaining constant, $d \propto p$.

Again, at constant pressure $v \propto T$; hence, p remaining constant, $d \propto 1/T$.

$\therefore$ $d \propto p/T$ where both T and p vary, i.e., $d = \text{constant} \times p/T$.

$\therefore$ $p/dT = \text{constant}$, $\qquad \therefore$ $p_1/d_1T_1 = p_2/d_2T_2$.

The density of a gas, also called its **normal density,** is the weight in grams of 1 litre measured at a temperature of 0°C, and under a pressure of 760 mm. of mercury.

One litre of hydrogen at N.T.P. weighs 0.089873 *gram.*

Normal temperature and pressure.—In order to compare the results on gaseous volumes measured under different conditions it is necessary to refer to some standard conditions of temperature and pressure under which the volumes are reduced. These standard data are 0°C and a pressure of 760 mm. of mercury. They are *called standard* (or *normal*) *temperature* and *pressure,* and are generally written as *S.T.P.* (or N.T.P.).

Saturation Pressure.—A little ether, when, exposed to air, passes rapidly into the vapour state by quick evaporation while mercury remains as it is, under a similar condition, without evaporation. Ether is said to be a *volatile* and mercury a *non-volatile liquid.* Liquids differ in their volatility : ether is more volatile than water. Vapours of liquids also exert pressure just like gases. When a closed space contains the maximum amount of vapour of a liquid at a certain temperature, the space is said to be *saturated* with the vapour and the pressure it then exerts is its *saturated vapour pressure.* The saturated vapour pressure of a liquid is constant at a certain temperature but is independent of the volume change. Just as there are unsaturated and supersaturated solutions, so there are unsaturated and supersaturated vapours. Saturated vapours do not obey Boyle's and Charles's laws but the unsaturated vapours do.

Dalton's law of partial pressures.—In a mixture of gases which do not react chemically, the total pressure exerted by the mixture is the sum of the *partial pressure* of each gas—the partial pressure is the pressure each gas would exert if it were *separately* confined in the entire volume occupied by the mixture. in the same temp This is Dalton's law of partial pressures.

Suppose a vessel of volume v contain n_1 and n_2 moles respectively of two gases A and B under a pressure p and at a given temperature T. Let p′ and p″ be the partial pressures of the two gases, i.e., p = p′ + p″.

v = v_1 (volume of gas A) + v_2 (volume of gas B).

By Boyle's law, $p'v = pv_1$, and $p''v = pv_2$,

$$\therefore\ p' = \frac{v_1}{v}p = \frac{v_1}{v_1+v_2}p\ ;\ p'' = \frac{v_2}{v}p = \frac{v_2}{v_1+v_2}p.$$

$$\text{Also, } p'v = n_1RT\ ;\ p''v = n_2RT \longrightarrow \frac{p'}{p''} = \frac{n_1}{n_2}$$

$$\therefore\ (p'+p'')v = (n_1+n_2)RT, \text{ i.e., } pv = (n_1+n_2)RT,$$

$$\therefore\ p' = \frac{n_1}{n_1+n_2}\cdot p\ ;\ p'' = \frac{n_2}{n_1+n_2}p. \longrightarrow \text{ or, } \frac{p'}{p'+p''} = \frac{n_1}{n_1+n_2}$$

Alternatively let two gases of volumes v_1 and v_2 at pressure p_1 and p_2 respectively are mixed together ; let the volume after mixing be v, i.e., $v = v_1+v_2$. Let the total pressure of the mixture be p, and the partial pressures of the two gases p′ and p″ respectively ; hence p = p′ + p″.

By Boyle's law, $p'v = p_1v_1$; $p''v = p_2v_2$.

$$\therefore\ p' = \frac{v_1}{v}p_1 = \frac{v_1}{v_1+v_2}p_1\ ;\ p'' = \frac{v_2}{v}\cdot p_2 = \frac{v_2}{v_1+v_2}\cdot p_2.$$

Pressure of gases collected over water.—When a gas is collected over water in a jar, the total pressure inside the jar is equal to the atmospheric pressure, when the levels of water inside and outside the jar are the same. Since the gas collected is *moist and saturated with water vapour* i.e., it is a mixture of gas and water vapour, the atmospheric pressure (P mm. of mercury) is equal to the sum of the partial pressure of the dry gas (p mm of mercury) and the partial pressure of saturated water vapour, also known as aqueous tension (f mm. of mercury) at the temperature at which the gas is collected.

Stated in symbols, $P = p+f$; $\therefore\ p = (P-f)$,

i.e., pressure of dry gas = atmospheric pressure − aqueous tension at t°C.

t°C is the temperature at which the gas is collected.

Let the volume of a moist gas at t°C = v c.c. ;
the barometric pressure = P mm. of mercury ;
the aqueous tension at t°C = f mm. of mercury.
∴ the pressure of dry gas = (P−f) mm. of mercury.

Let the gas occupy a volume of v′ c.c. at N.T.P., then by Boyle's law,

$$\frac{v'\times 760}{273} = \frac{v(P-f)}{273+t}, \text{ or } v' = \frac{v.(P-f).273}{(273+t).760}$$

Another case arises when the levels of water inside and outside the jar are not the same. Suppose the water stands at a height h mm. above the water in the trough, then the atmospheric pressure = the pressure of dry gas + the aqueous tension + the pressure of h mm. of water. Symbolically stated, $P = p+f+h/13{\cdot}59$,
since the density of mercury is 13.59 gm. per c.c.

$$\therefore\ p = (P-f-h/13{\cdot}59).$$

Kinetic Theory of Gases.—The physical properties of gases may be explained in terms of the kinetic theory which is based on the following assumptions :

(i) A gas is composed of a large number of minute particles, called *molecules*, which are moving at random in space, continually colliding with one another or with the walls of the containing vessel.

(ii) The molecules are supposed to be *perfectly elastic*, i.e., they possess energy only in virtue of their translational motion and suffer no loss of translational energy due to inter-molecular collisions.

(iii) The molecules are so small that their actual volume is negligible compared to the total volume of the gas.

(iv) The actual volume of the molecules is very small compared to the space they occupy, i.e., the total volume of the gas, and the distances between them are so large that inter-molecular forces are negligible, i.e., there is no force of attraction or repulsion acting between the molecules.

(v) The pressure exerted by a gas is due to the impact of the molecules on the walls of the containing vessel, while the gaseous diffusion is due to their random motion.

(vi) Two gases are at the same temperature when the average kinetic energy of the individual molecule of each gas (which is a measure of its temperature) is the same.

All the gas laws, viz., Boyle's law, Charles's law, Avogadro's law and Graham's law of diffusion, find adequate explanations in terms of the kinetic theory of gases from which they can be deduced mathematically.

Diffusion of gases.—The molecules of a gas are not in a state of rest, but are really in a state of ceaseless chaotic motion. Thus, when some chlorine gas is led into the bottom of a gas-jar (which presumably contains air), it is found that the gas quickly spreads out into the jar so that its contents appear uniformly greenish-yellow, although it is about two and a half times as heavy as air ; this is because its molecules are in rapid and random motion.

When a gas-jar is filled with hydrogen and held mouth downwards, the hydrogen rapidly passes out and air enters, as is evident from the observation that if a lighted paper is applied to the jar, it is found that no trace of the gas remain—the hydrogen, if present, would have burnt with a pale blue flame. This is another illustration of the random motion of the molecules ; the movement has taken place in opposition to gravity, since air, the heavier gas, moves upward and hydrogen, the lighter gas, moves downward.

Exactly for the same reasons, when a jar of hydrogen is inverted over a jar of carbon dioxide which is twenty-two times as heavy as hydrogen, the molecules of the two gases so intermix together that a perfectly uniform mixture is obtained. *Such an intermixture of different non-reacting gases without the aid of outside agencies is due to the perpetual random motion of their molecules, and is known as the phenomenon of diffusion.* Regardless of densities, all gases possess the property of diffusion ; the phenomenon of diffusion is independent of gravity.

The foul smell of hydrogen sulphide in a chemical laboratory is an unmistakable proof of its diffusion in air. It is diffusion that spreads the fragrance of flowers. Tear gas pervades a locality while used in dispersing a chaotic mob.

Graham's law of diffusion.—A light gas diffuse more rapidly than a heavy gas.

At a given temperature and pressure the rate of diffusion of a gas is inversely proportional to the square root of its density.

Thus, oxygen is 16 times as heavy as hydrogen, and therefore diffuses $\sqrt{16} = 4$ times as slowly.

Carbon dioxide is 22 times as heavy as hydrogen, and therefore diffuses $\sqrt{22}=4.69$ times as slowly.

Mathematically, the law is stated as : $r \propto 1/\sqrt{d}$.

Consequently, $\frac{r_1}{r_2}=\sqrt{\frac{d_2}{d_1}}$

where d_1 and d_2 are the densities of two gases, for which the rates of diffusion under identical conditions are r_1 and r_2.

The rate of diffusion means the volume-rate, and is measured by the volume of a gas diffusing per unit of time, and is usually expressed as :

$$\text{rate of diffusion} = \frac{\text{volume of diffused gas in c.c.}}{\text{time in seconds.}}$$

Experiments illustrating diffusion.—The phenomenon of diffusion may be demonstrated with the following experiments :—

(i) A porous clay pot is fitted by means of a rubber bung to the longer limb of a bent tube containing some coloured liquid, such as a solution of potassium permanganate—the shorter limb of the tube ending in a fine jet (fig. 33). On inverting a beaker full of hydrogen over the porous pot, it is found that the coloured liquid spurts out through the jet in the form of a fountain. The explanation is simple. The molecules of hydrogen, the lighter gas, diffuse into the pot more rapidly, and therefore in larger numbers, than the molecules of air, the heavier gas, can pass out ; consequently, there occurs an increase of pressure inside the pot, and hence the liquid is forced out.

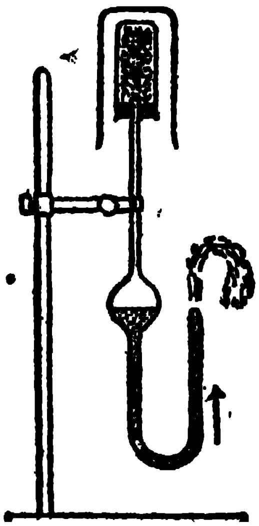


Fig. 33

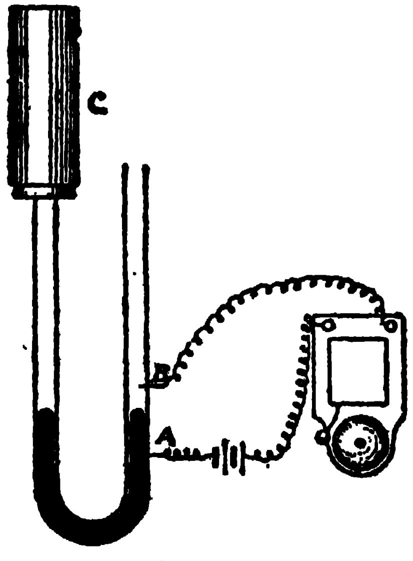


Fig. 34

(ii) One limb of a glass U-tube (fig. 34) is connected through a rubber bung to a porous pot C, containing air. The other limb has two platinum wires fused into it, A being in contact with the mercury in the U-tube, while B is *just above it.* On inverting a jar of hydrogen over C, the lighter hydrogen diffusing more quickly into the porous pot than the air out of it, forces the mercury level in the right limb higher and higher up, ultimately causing it to touch B—the bell starts ringing at this moment as A and B form a circuit with an electric bell and battery. The *marsh gas detector* in coal mines work on the same principle. In the event of any marsh gas escaping from a coal fissure into the mine, the level of mercury in the right limb rises and establishes a contact between the battery and the bell, which starts ringing—this serves as a warning to the miners.

Diffusion finds *applications* (i) in determining the relative densities and molecular weights of gases, particularly when available in small quantities only :

(ii) in the separation of two gases of different densities—the process is called *atmolysis* :

(iii) in *marsh gas detectors* in coal mines. The spread of foul gases in air by diffusion is the cause for the necessity of good ventilation in rooms and mines which greatly dilutes the deleterious effect of such gases.

Effusion of Gases.—Effusion is a process in which a gas is forced under pressure through a small aperture in a thin metal plate exposed to the air.

Graham's law applies equally to the rates of diffusion and effusion. The law holds good whether the gas densities are expressed as normal or relative densities. Since twice the relative density of any gas is its molecular weight.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

where M_1 and M_2 are the molecular weights of the two gases.

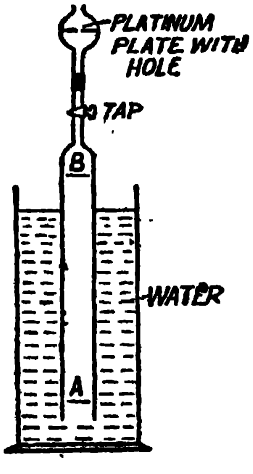


Fig. 35

The process of effusion is utilised to compare the molecular weights of different gases in Bunsen's *effusiometer*. It consists of a glass tube open at the lower end and placed in a cylinder of water (fig. 35). The upper end of the tube is closed by a stopcock which is attached to a glass tube closed by a thin platinum plate in which a very fine hole has been pierced—the stopcock communicates with the free air through this fine aperture. The tube is filled with a gas under examination to a level below A and the tap is opened—the gas streams out through the hole and the time taken for the water level to pass from A to B is noted by a stop watch. The experiment is repeated with a gas of known density, say oxygen.

Let t_1 and t_2 are times of effusion of equal volumes of two gases of densities d_1 and d_2 and molecular weights M_1 and M_2.

Let the volume of gases effused = v c.c. and r_1 and r_2 are the rates of effusion, then $r_1 = v/t_1$ and $r_2 = v/t_2$.

$$\therefore \quad \frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

For gases soluble in water, mercury is the liquid used.

Exercises

1. A gas occupies 100 c.c. at a pressure of 340 mm. of mercury. What will be the volume at a pressure of 1000 mm., assuming the temperature to be constant ?

We use Boyle's law : pressure × volume = constant ;

$\therefore \quad 100 \times 340 = 1000 \times x$, whence $x = 34$ c.c.

2. A litre of gas is measured at 20°C. At what temperature will its volume be 1750 c.c. ?

We use Charles's law : $\frac{v_1}{T_1} = \frac{v_2}{T_2}$;

$v_1 = 1000$ c.c. ; $T_1 = 273 + 20 = 293$; $v_2 = 1750$ c.c. ; $T_2 = x$.

$\therefore \quad \frac{1000}{293} = \frac{1750}{x}$ or $x = 512.8°$ absolute.

Let the temperature be t°C, then

$T_2 = (273 + t)°$ absolute $= 512.8°$ abs. or $t = 239.8°$C.

3. Correct a volume of 234 c.c. measured at 756 mm. and 12°C to standard conditions.

Standard temperature is 0°C = 273° absolute.

Standard pressure is 760 mm. of mercury.

We apply the general gas equation : $\frac{p_1v_1}{T_1} = \frac{p_2v_2}{T_2}$

$p_1 = 756$ mm. ; $v_1 = 234$ c.c. ; $T_1 = 273+12 = 285$;

$p_2 = 760$ mm. ; $v_2 = x$; $T_2 = 273$;

$$\therefore \quad \frac{756 \times 234}{285} = \frac{v_2 \times 760}{273} \text{ whence } v_2 =$$

4. 110 c.c. of hydrogen were collected over water at 18°C and 740 mm. pressure. Calculate the volume of the gas at N.T.P. (a) taking account of pressure of water vapour. (15.4 mm. at 18°C), (b) neglecting the effect of the water vapour.

(*a*) From the relation $\frac{v_1 760}{273} = \frac{v(P-f)}{(273+t)}$

$$v_1 = \frac{v(P-f)273}{(273+t)760} = \frac{110.(740-15.4)273}{(273+18)760} = 98.4 \text{ c.c.}$$

$$\frac{v_1 760}{273} = \frac{v.P}{(273+t)} \text{ (aqueous tension neglected)}$$

$$\therefore \quad v_1 = \frac{v.P.273}{(273+t).760} = \frac{110.740.273}{(273+18).760} = 100.5 \text{ c.c.}$$

5. If the density of hydrogen is 0.09 gm. per litre at N.T.P., what is its density at 15°C and the pressure 750 mm. ?

$$\frac{P_1v_1}{T_1} = \frac{P_2v_2}{T_2} \text{ becomes } \frac{P_1}{d_1T_1} = \frac{P_2}{d_2T_2}$$

$$\therefore \quad \frac{760}{0.09 \times 273} = \frac{750}{d_2 \times (273+15)}, \text{ whence } d_2 = 0.0842 \text{ gm. per litre.}$$

6. A gas is collected over water in a jar. The volume measured is 270 c.c. The height of water in the jar is 2.72 cm. The temperature of the gas is 27°C. Aqueous tension at 27°C is 26.75 mm., and atmospheric pressure is 756.75 mm. Calculate the volume of the gas at N.T.P. Density of mercury is 13.6 gm. per c.c.

Pressure of water column in the jar = 27.2/13.6 = 2 mm.

∴ Pressure of *moist* gas collected = 756.75 − 2 = 754.75 m.m.

∴ pressure of *dry* gas = 754.75 − 26.75 = 728 mm.

$$\therefore \quad \frac{v \times 760}{273} = \frac{270 \times 728}{(273+27)}, \text{ or } v = 235.4 \text{ c.c.}$$

7. A spherical balloon of 21 cm. diameter is to be filled up with hydrogen at N.T.P. from a cylinder containing the gas at 20 atmospheres and 27°C ; if the cylinder can hold 2.82 litres of water, calculate the number of balloons that can be filled up.

Volume of a sphere = $^4/_3\pi r^3$.

Volume of spherical balloon = $^4/_3 \times {}^{22}/_7 \times ({}^{21}/_2)^3 = 4851$ c.c.

Capacity of the cylinder = 2820 c.c.

$$\therefore \quad \text{volume of } H_2 \text{ at N.T.P.} = \frac{2820 \times 20 \times 273}{300 \times 1} = 51330 \text{ c.c.}$$

Of this total volume, 2820 c.c. of H_2 (at 1 atmosphere) remain in the cylinder, so that only (51330−2820) = 48510 c.c. of the gas are available for filling the balloons.

∴ number of balloons = 48510/4851 = 10 only.

35. At 17°C 40 gm. of electrolytic gas are contained in a 60 litre gas-holder. What are the partial pressures of hydrogen and oxygen ?
Hydrogen, 0.8807 atmos. ; oxygen, 0.4403 atmos.

36. The weight of 1 litre of a certain gas at N.T.P. is 1.44 gm. How many c.c. of hydrogen (normal density of 0.09) will diffuse in the same time that 20 c.c. of the gas diffuse under the same conditions ? 80 c.c.

37. If 374.2 c.c. of hydrogen diffuse through a crack in 10 seconds, how much ethylene (density 14) will diffuse in the same time ? 100 c.c.

38. Time of effusion of the same volume of pure oxygen and a mixture of oxygen and ozone are 100 and 105 seconds respectively. Find the percentage by volume of ozone (density 24) in the mixture. 20.5

39. Explain what is meant by diffusion of gases. State Graham's law of diffusion. Describe an experiment to illustrate the phenomenon of diffusion. The speeds of diffusion of carbon dioxide and ozone were found by Soret to be 0.29 : 0.27. Determine the density of ozone, that of carbon dioxide being 22.
Allahabad Inter. Board, '46 ; 25.37

40. In 50 seconds 300 c.c. of oxygen diffuse through a porous plate. How long will it take 500 c.c. of chlorine to diffuse through the same plate ? Take the molecular weights of oxygen and chlorine to be 32 and 72 respectively.
125 *seconds*

41. Ladenburg found that ozonised oxygen containing 86.16 per cent ozone by volume required 430 seconds to diffuse, whereas the same volume of oxygen required 367.4 seconds under the same conditions. Find the density of ozone. 22.9

42. 220 c.c. of a gas are collected over mercury in a tube of which the top is closed by a plug of plaster of Paris. The gas diffuses on standing, and the mercury level then stands at 297 c.c. Calculate the molecular weight of the gas if the amount of it which diffused out was 126 c.c. Density of air = 14.4. 74.76

43. 300 c.c. of gas measured at 740 mm. pressure are passed into a vessel of 500 c.c. capacity, which has been previously evacuated. What will be the pressure in the new vessel ? 444 mm.

44. What is Graham's law of diffusion ? Describe an experiment to show that hydrogen diffuses more rapidly than air. 16 c.c. of hydrogen were found to diffuse in 30 seconds. What volume of sulphur dioxide would diffuse in the same time under the same conditions. U. P. Board, '51 ; 2.8 c.c.

45. A soap bubble of 8 cm diameter, containing air at 27°C and 760 mm. pressure, is expanded until its radius is 8 cm., the temperature and pressure remaining constant. How many c.c.'s of air at N.T.P. are required for the expansion ? 1709

46. 40 c.c. of oxygen measured at N.T.P. were confined in a tube of cross-section 1.2 sq. cm. sealed at upper end, and standing in a trough of mercury, the column of which stood at a height of 15.6 cm. The pressure of the atmosphere was found to be 756 mm. and the temperature of the laboratory was 31°C. Calculate the length of the tube containing the gas. 47 cm.

47. A cylinder of 10 litres capacity which contains oxygen under a pressure of 20 atmospheres at 27°C, is leaking at a constant rate of 5 c.c. of the gas (N.T.P.) per minute. Calculate the fall in pressure (in atmospheres) in the cylinder at the end of 10 hours. 0.23 *atmospheres*

48. How much additional pressure in atmospheres is to be applied to compress a gas contained in a spherical balloon at 1 atmosphere in order to make it fill another balloon with 1/4 the diameter ? 63 *atmospheres*

49. A given mass of a gas occupies a volume of 2.5 litres at 0°C and 76 cm. pressure of mercury. Find its volume at 546°C and 150 cm. pressure of mercury.
3.8 litres

VII

THE LAWS OF STOICHIOMETRY & ATOMIC THEORY

As a result of the *quantitative* study of chemical changes the following **Laws of Chemical Combination by weight,** also called the **Laws of stoichiometry,** were arrived at towards the end of the 18th and the beginning of the 19th century.

(i) *The law of conservation of mass,*
(ii) *The law of constant proportions.*
(iii) *The law of multiple proportions.*
(iv) *The law of reciprocal proportions.*

Combination of elements to form compounds and chemical reactions in general are governed by these laws. These laws are purely experimental and are not based on any theory.

The law of conservation of mass.—The law was experimentally arrived at by Lavoisier in 1774.

In a chemical change the total mass of the reacting substances is equal, within the limits of experimental error, to the total mass of the products of the reaction (*page* 12).

Since there is no gain or loss of matter accompanying a chemical change, every correctly balanced chemical equation is based on this law.

The law of constant proportions, also called **the law of definite proportions,** was discovered by the French chemist Proust in 1799. The law states that :

The same compound always contains the same elements combined together in the same definite proportions by weight.

Irrespective of any method of preparation or source, water always contains the elements hydrogen and oxygen only, in the same proportion of 1.008 to 8 parts by weight ; common salt does contain the elements sodium and chlorine only—always in the ratio of 23 to 35.5 parts by weight ; carbon dioxide is made up of the elements carbon and oxygen only and always in the fixed ratio of 3 to 8 parts by weight. Since elements combine in definite ratios by weight, *the composition of a pure chemical compound is definite* and is independent of its method of preparation.

The law is implied in the very definition of a compound. According to the law of definite proportions, a particular compound has a fixed and definite chemical composition, but the converse is not always true : the same elements, for example, may combine in the same mass proportion to form different compounds, each with characteristic properties—these different compounds of the same composition are called *isomers* and the phenomenon is known as *isomerism* (page 60).

The law may be verified by preparing the same compound in different ways and analysing the samples obtained. The law received its confirmation from the classical experimental works of Stas (1865).

The analysis of black oxide of copper.—Different samples of the oxide are prepared by :

(i) dissolving some copper turnings in 1 : 1 nitric acid and evaporating to dryness ; the green copper nitrate that is formed, decomposes on strong heating to yield black cupric oxide.

(ii) dissolving some copper turnings in nitric acid and adding an excess of sodium carbonate solution, when blue copper carbonate is precipitated ; this is filtered, washed, dried, and ignited to give cupric oxide.

(iii) dissolving some copper in nitric acid as before and adding an excess of sodium hydroxide solution, when blue copper hydroxide is precipitated ; the precipitate on boiling, is converted into hydrated copper oxide ; this is filtered, washed, dried and ignited to yield cupric oxide.

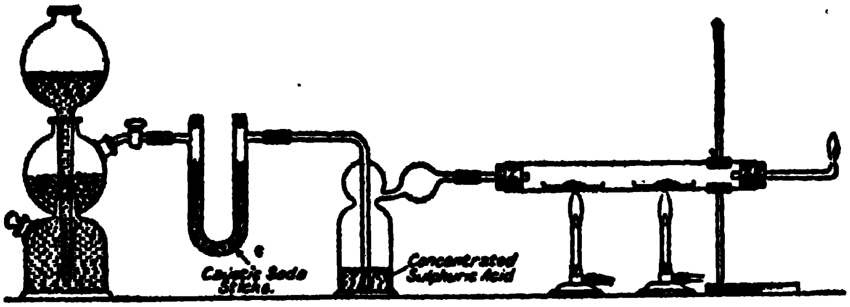


Fig. 36

A small amount of each of the three different samples of cupric oxide, say about 1 gm., is put in a tared porcelain boat, and weighed again. The boat with its contents is then carefully heated in a stream of hydrogen gas in a long, hard glass tube, when cupric oxide is reduced to rose-red metallic copper (fig. 36). The boat with the reduced copper is then cooled in a slow stream of hydrogen in the tube, and weighed again. The results are entered as follows :

	gm.
Weight of the boat	a
Weight of the boat + copper	b
Weight of the boat + cupric oxide	c
Weight of cupric oxide	(c−a)
Weight of copper	(b−a)
Weight of oxygen	(c−b)

$\therefore$ % of Cu = (b−a) × 100/(c−a) ; % of O_2 = (c−b) × 100/(c−a)

The actual result is : % of Cu = 79.89 ; % of O_2 = 20.11.

In other words, in each case the copper oxide contain copper and oxygen in the ratio of 63.57 to 16 parts by weight.

The analysis of silver chloride.—Silver chloride is prepared by :

(i) dissolving a known amount of silver, say about 0.5 gm., in 1 : 1 nitric acid and adding an excess of hydrochloric acid to the silver nitrate which is formed—the silver chloride which precipitated, is filtered, washed, dried and weighed.

(ii) heating a known weight of silver, about 0.5 gm., in a current of chlorine gas ; about 0.5 gm. of silver is accurately weighed out in a tared porcelain boat and heated in a current of chlorine gas in a glass tube until the silver is completely converted into silver chloride—the boat with its contents is then cooled and weighed again. The results are entered as follows :—

	gm.
Weight of boat	a
Weight of boat + silver	b
Weight of boat + silver chloride	c
∴ Weight of silver	(b−a)
Weight of chlorine	(c−b)
Weight of silver chloride	(c−a)

∴ % of Ag = $(b-a)\times100/(c-a)$; % of Cl_2 = $(c-b)\times100/(c-a)$.

In each case it is found that silver and chlorine combine in the ratio of 107.88 to 35.457 parts by weight.

The law of multiple proportions.—This law was arrived at by Dalton in 1803 as a result of some theoretical reasoning about gases.

When two elements combine to form more than one compound, the several weights of one element which combine with a fixed weight of another element are in the ratio of small whole numbers.

Illustrations.—(i) Let us consider water and hydrogen peroxide. In water H_2O, 1.008 parts by weight of hydrogen combine with 8 parts by weight of oxygen ; in hydrogen peroxide, H_2O_2, 1.008 parts by weight of hydrogen combine with 16 parts by weight of oxygen. Hence, the same weight, 1.008 parts by weight of hydrogen unite with 8 and 16 parts by weight of oxygen in water and hydrogen peroxide respectively. 8 and 16 are in simple ratio of 1 : 2

Compound	*Composition by weight*		*Simple ratio of oxygen*
	Hydrogen	Oxygen	
Water	1.008	8	
Hydrogen peroxide	1.008	16	1 : 2

(ii) In the five oxides of nitrogen, nitrous oxide, nitric oxide, nitrogen trioxide, nitrogen tetroxide and nitrogen pentoxide, the weights of oxygen combining with a definite amount of nitrogen are in the ratio of 1 : 2 : 3 : 4: 5.

Oxdes of nitrogen	*Composition by weight*	
	Nitrogen	Oxygen
Nitrous oxide, N_2O	14	8(1×8)
Nitric oxide, NO	14	16(2×8)
Nitrogen trioxide, N_2O_3	14	24(3×8)
Nitrogen tetroxide, N_2O_4	14	32(4×8)
Nitrogen pentoxide, N_2O_5	14	40(5×8)

(iii) In the following hydrides of carbon, acetylene, ethylene, ethane and methane, 12 parts by weight of carbon combine with 1.008, 2×1.008, 3×1.008, and 4×1.008 parts of hydrogen respectively—these weights are in the ratio of 1:2:3:4.

Compound	*Composition by weight*	
	Carbon	Hydrogen
Acetylene, C_2H_2	12	1.008
Ethylene, C_2H_4	12	2×1.008
Ethane, C_2H_6	12	3×1.008
Methane, CH_4	12	4×1.008

(iv) The two oxides of copper, namely black cupric oxide and red cuprous oxide, illustrate the law.

Compound	*Composition by weight*		*Simple ratio of copper*
	Oxygen	Copper	
Cupric oxide, CuO	16	63.57	1 : 2
Cuprous oxide, Cu_2O	16	63.57×2	

(v) The three oxides of carbon also illustrate the law.

Compound	*Composition by weight* Oxygen	Carbon	*Simple ratio of carbon*
Carbon dioxide, CO_2	8	3	
Carbon monoxide, CO	8	6	1 : 2 : 3
Carbon suboxide, C_3O_2	8	9	

The law of reciprocal proportions.—The law was discovered by Richter in 1792, and is also called **the law of equivalent proportions** or **the law of combining weights.** The law states :

The weights of two or more elements which combine separately with a fixed weight of another element, are either the weights in which these elements combine with one another or are simple multiples of them.

In other words, the proportions in which any two elements unite with a third element are the proportions or a simple multiple or submultiple of the proportions in which they combine with each other.

Illustrations.—(*i*) Let us consider hydrogen, sodium, chlorine and their compounds sodium hydride, hydrogen chloride and sodium chloride.

Compound	*Composition by weight*	*Ratio of equivalents*
Sodium hydride, NaH	H : Na = 1 : 23	
Hydrogen chloride, HCl	H : Cl = 1 : 35.5	Na : Cl : 23:35.5
Sodium chloride, NaCl	Na : Cl = 23 : 35.5	

With respect to combination with hydrogen, the equivalents of sodium and chlorine are 23 and 35.5 respectively. Sodium and chlorine should, therefore, combine in the ratio of 23 : 35.5. In sodium chloride the ratio is 23 : 35.5.

(*ii*) Consider the elements carbon, hydrogen and oxygen.

Compound	*Composition by weight*	*Ratio of equivalents*
Methane, CH_4	H : C = 1 : 3	
Water, H_2O	H : O = 1 : 8	
Carbon dioxide, CO_2	C : O = 3 : 8	C : O = 3 : 8
Carbon monoxide, CO	C : O = 3 : 4	

The equivalents of carbon and oxygen are 3 and 8 respectively. Carbon and oxygen should combine in the ratio of 3 : 8 by weight or in simple multiple or submultiple of this ratio. In carbon dioxide the ratio is 3 : 8 and in carbon monoxide it is 3 : 4 (4 is a submultiple of 8).

(*iii*) The following compounds also illustrate the law :

Compound	*Composition by weight*	*Ratio of equivalents*
Carbon dioxide, CO_2	C : O = 3 : 8	
Sulphur dioxide, SO_2	S : O = 8 : 8	C : S = 3 : 8
Carbon disulphide, CS_2	C : S = 3 : 16	

Carbon and sulphur should combine in the ratio of 3 : 8 or in their simple multiples ; in carbon disulphide the ratio is 3 : 16 ; 16(2×8) is a multiple of 8.

(*iv*) Examine the following compounds of carbon, hydrogen and oxygen.

Compound	*Composition by weight*	*Ratio of equivalents*
Water, H_2O	H : O = 1 : 8	
Carbon dioxide, CO_2	C : O = 3 : 8	
Methane, CH_4	H : C = 1 : 3	H : C = 1 : 3
Ethylene, C_2H_4	H : C = 1 : 6	
Acetylene, C_2H_2	H : C = 1 : 12	

Hydrogen and carbon should combine in the ratio of 1 : 3 by weight or in their simple multiples ; in methane the ratio is 1 : 3, in ethylene 1 : 6, and in acetylene 1 : 12 ; 6 and 12 are multiples of 3.

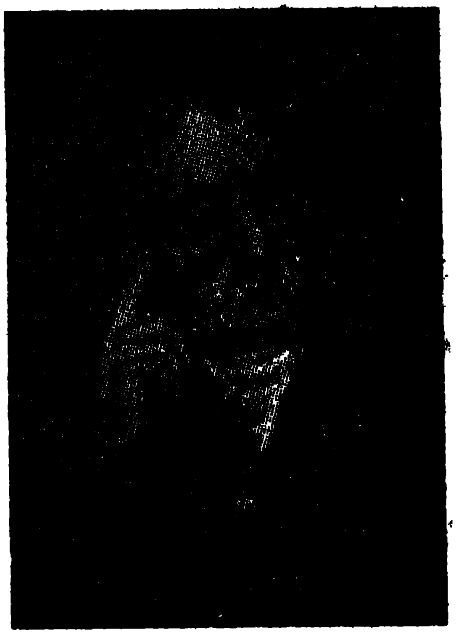
The atomic theory.—The idea that matter is composed of ultimately indivisible particles is as old as natural philosophy. It has been vaguely supposed from very early times by the ancient philosopher Kanad and the Greek philosophers Leukippos and Demokritos (about 450 B.C.) that matter is composed of very minute indivisible particles, called atoms. Their metaphysical speculation was developed by the English scientist John Dalton in 1803 into a scientific theory which asserts that :

(*i*) *All elements are composed of very minute particles of matter called atoms, which remain undivided in all chemical changes.*

(*ii*) *Each kind of atom has a definite weight, but the atoms of different elements differ in weight.*

(*iii*) *All the atoms of the same element are identical with one another in all respects, particularly in weight.*

Atoms of different elements are themselves different having different properties, such as weight, chemical affinity, etc.



John Dalton (1766—1844).
Fig. 37

(*iv*) *Chemical combination takes place by the union of atoms of the elements in simple numerical ratios,* 1 : 1, 1 : 2, 2 : 3, *etc.*

The atom, therefore, is the smallest particle of an element which can take part in a chemical change.

It is not out of place to mention here that according to the original assumption of Dalton's atomic theory an atom was the smallest particle of all kinds of matter, be it an element or a compound. The smallest particle of an element was called a '*simple atom,*' and that of a compound was called a '*compound atom*'. A 'compound atom' was formed by the union of atoms of different elements in simple proportions.

Limitations of Dalton's Theory.—The enunciation of Dalton's atomic theory gave a powerful stimulus to experimental researches in the beginning of the 19th century. Though *each kind of atom has a definite weight,* the theory provided no means of determining even the relative weights of atoms. He asserted that *the combining weight of an element was its atomic weight* and that if only one compound of two elements were known, it was formed of one atom of each element. In water, for example, 1 part by weight of hydrogen unites with 8 parts by weight of oxygen ; hence assuming that water contains 1 atom each of hydrogen and oxygen (the formula for water being HO as Dalton assumed), the atomic weight of oxygen comes out to be 8, that of hydrogen being taken to be one. Berzelius, on the other hand, assumed that water contained 2 atoms of hydrogen and 1 atom of oxygen, its formula being H_2O ; and hence :

$$\frac{1}{8} = \frac{2 \times \text{atomic weight of hydrogen}}{1 \times \text{atomic weight of oxygen}}$$

atomic weight of oxygen = 16, (at. wt. of H = 1)

Hence, *atomic weights can only be determined if the ratio in which atoms of elements combine be known.*

$$\text{In general, } \frac{p}{q}=\frac{m}{n}\cdot\frac{a}{b},$$

where p and q are the combining weights (i.e., the equivalent weights) of two elements ; a and b their atomic weights, and m and n the number of atoms of each element which combine.

Let p, m and a denote the equivalent weight, number of atoms, and atomic weight of hydrogen respectively, hence $p = 1$ and $a = 1$.

$\therefore\ \frac{1}{q}=\frac{m}{n}\cdot\frac{1}{b}$ or $b=\frac{m}{n}\cdot q$; where $\frac{m}{n}$ = the ratio of number of atoms of hydrogen to those of another element. But since one atom of hydrogen never combines with less than one atom of any other element, it has the least combining capacity and is taken as unity. Hence m/n represents the number of atoms of hydrogen with which one atom of the element combines ; hence $m/n = v$, the valency of the element.

$\therefore$ $b = v \times q$, i.e., atomic weight = equivalent weight × valency.

The atomic theory and the stoichiometric laws.—The laws of chemical combination by weight were all explained by the atomic theory—it being the *only* piece of evidence for the theory when it was proposed. But since then convincing physical demonstrations of real existence of atoms have placed the theory beyond all reasonable doubt.

(i) **Law of conservation of mass.**—The weight of a chemical system is the sum of the weights of all the atoms in it. Chemical change involves merely a re-arrangement of atoms whose mass is constant and which remains unaltered during any chemical process. Hence no change of mass results in the re-grouping of atoms in a chemical reaction. That is, the weight of the system remains *constant.*

(ii) **Law of definite proportions.**—According to the atomic theory a compound is formed by the union of atoms in a simple fixed ratio.

Let x atoms of an element A unite with y atoms of another element B to form the molecule of a compound AxBy. Let the atomic weights of the elements A and B be a and b grams respectively. According to Dalton's atomic theory, the atomic weight of an element is constant and hence the atomic weights a and b are constant ; and also the ratio x to y is fixed for the compound AxBy. Hence in all samples of AxBy, the ratio

$$\frac{\text{weight of A}}{\text{weight of B}}=\frac{x\times\text{atomic weight of A}}{y\times\text{atomic weight of B}}=\frac{x\times a}{y\times b}=\text{constant.}$$

That is, the compound AxBy has a constant composition. Hence the deduction of the law of definite proportions.

(iii) **Law of multiple proportions.**—Let the two elements A (at. wt. a) and B (at. wt. b) combine to form the compounds AxBy. Am Bn and Ap Bq in the simple ratio of atoms, $x:y$, $m:n$ and $p:q$ respectively. The proportions by weight of A and B in these compounds are :

Compound	Proportion by weight of A and B.
Ax By	ax : by or a : by/x
Am Bn	am : bn or a : bn/m
Ap Bq	ap : bq or a : bq/p

Let by/x = d, bn/m = e, bq/p = f.

The different weights of B combining with a fixed weight, namely *a* parts by weight of A are d, e and f ; their ratio is :

$$d : e : f = by/x : bn/m : bq/p = ymp : xnp : qxm.$$

Now, since x, y, m, n, p and q are small integers, their products are also small whole numbers. Therefore, the ratio ymp : xnp : qxm is a ratio of small whole numbers and hence the law is deduced.

Taking the hydrocarbons acetylene C_2H_2, ethylene C_2H_4, and methane CH_4 for AxBy, AmBn and ApBq respectively, $x = 2$, $y = 2$, $m = 2$, $n = 4$, $p = 1$, $q = 4$, and the ratio ymp : nxp : qxm = 1 : 2 : 4.

(iv) **Law of reciprocal proportions.**—Consider the elements A, B and C, their atomic weights being *a*, *b*, and *c* units respectively. Let A separately combine with B and C to form A*x*B*y* and A*m*C*n* in simple ratio of atoms, *x* : *y* and *m* : *n*, respectively ; let *p* atoms of *B* combine with *q* atoms of C to form B*p*C*q*. The proportions by weight of A, B and C in these compounds are :

Compound	Proportion by weight
Ax By	ax : by or a : by/x
Am Cn	am : cn or a : cn/m
Bp Cq	bp : cq

Let by/x = d and cn/m = e. The weights of B and C combining with a definite weight, namely *a* parts by weight of A are d and e. According to the law of equivalent proportions B and C should combine in the ratio of d : e or in simple multiple of this ratio. In BpCq B and C combine in the ratio of bp : cq by weight. Therefore,

bp : cq should be equal or simply related to d : e.

Now, $d : e = by/x : cn/m = bym : cxn$,

$$\text{also } \frac{bp}{cq} = \frac{bp \times ymxn}{cq \times ymxn} = \frac{bym \times pxn}{cxn \times qym} = \frac{d \times pxn}{e \times qym}$$

Since x, y, m, n, p and q are small whole numbers, their products are also small whole numbers. Therefore bp/cq is either equal to d/e (when pxn = qym) or simply related to it, since pxn is a whole number, and so also qym, and hence the law.

Taking CH_4, CO_2 and H_2O for A*x*B*y*, AmCn and BpCq respectively, $x = 1$, $y = 4$, $m = 1$, $n = 2$, $p = 2$ and $q = 1$. ∴ pxn = 4 and qym = 4.

That is bp/cq is equal to d/e.

The law of gaseous volumes.—*Under the same conditions of temperature and pressure the volumes of gases entering into a chemical reaction bear a simple ratio to one another and also to the product, if gaseous.* combination

This law was arrived at by the French scientist Gay Lussac in 1808 from a study of the reacting volumes of gases.

Experiments show that under the same conditions of temperature and pressure :

(i) One volume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride ; and hence the ratio of their volumes is 1 : 1 : 2.

(ii) 2 volumes of hydrogen combine with one volume of oxygen to form two volumes of steam. Therefore, the required ratio is 2 : 1 : 2.

(iii) 1 volume of nitrogen combines with 3 volumes of hydrogen to yield 2 volumes of ammonia ; consequently, the ratio is 1 : 3 : 2.

(iv) 1 volume of nitrogen combines with 1 volume of oxygen to produce 2 volumes of nitric oxide, and hence the ratio is 1 : 1 : 2.

Gay Lussac's law of gaseous volumes is, therefore, a generalisation of experimental results.

Adoption of Avogadro's hypothesis.—Dalton's atomic theory *assumes* that : *Elements combine in simple ratio by atoms :* While Gay Lussac's law of gaseous volumes, *experimentally arrived at*, asserts that : *Gases combine in simple ratio by volume.* Consequently for chemical reaction between gases, there must be some simple relation between the *volumes* of gases and the number of *atoms* contained in them.

The Swedish chemist, Berzelius, correlated the Gay Lussac's law and Dalton's atomic theory in the hypothesis :

Equal volumes of all gases at the same temperature and pressure contain the same number of atoms.

The term *atom* included Dalton's '*compound atoms.*'

But when applied to interpret experimental facts, Berzelius's hypothesis led to a conclusion which was in direct conflict with the fundamental assumption of Dalton's atomic theory *that atoms are indivisible.* Thus, it is found by experiments that one volume of hydrogen unites with one volume of chlorine to form 2 volumes of hydrogen chloride.

Let *n* represent the number of atoms present in one volume of hydrogen. Then, by Berzelius's hypothesis, *n* atoms of chlorine are also present in one volume of chlorine, and 2*n* *compound atoms* of hydrogen chloride are present in two volumes of it. Hence,

n atoms of hydrogen unite with *n* atoms of chlorine to give 2*n* 'compound atoms' of hydrogen chloride.

∴ 1 atom of hydrogen unites with 1 atom of chlorine to give 2 'compound atoms' of hydrogen chloride.

or $\frac{1}{2}$ atom of hydrogen unites with $\frac{1}{2}$ atom of chlorine to give 1 'compound atom' of hydrogen chloride.

The result goes against the atomic theory, since atoms, according to Dalton's atomic theory, are indivisible. Berzelius's hypothesis was therefore, vigorously disputed by Dalton. There was utter confusion for some time in the realm of chemistry, and the hypothesis was ultimately rejected. Dalton's atomic theory could not be reconciled with Gay Lussac's law, since the former made no distinction between the ultimate particles of elements and compounds. The difficulty was, however, overcome in a surprisingly simple way by the Italian scientist Amadeo Avogadro in 1811.

Gay Lussac's law and Dalton's atomic theory were correctly ated by Avogadro who distinguished between two kinds of te particles of matter, an atom and a molecule.

An atom is the smallest particle of an element which can take part in a chemical change.

A molecule is the smallest particle of an element or a compound which can exist in the free state.

Consequently, the smallest unit of matter which can exist in a gas is not an atom but a molecule. So the volume of a gas is related to the number of molecules present in it. This is stated in Avogadro's hypothesis.

Avogadro's hypothesis.*—*Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.*

The hypothesis correctly explains experimental facts. Thus it is found experimentally that :

1 volume of hydrogen unites with 1 volume of chlorine to give two volumes of hydrogen chloride.

Let n be the number of molecules present in 1 volume of hydrogen. Hence, by Avogadro's hypothesis :

n molecules of hydrogen unite with n molecules of chlorine to give $2n$ molecules of hydrogen chloride.

or 1 molecule of hydrogen unites with one molecule of chlorine to give 2 molecules of hydrogen chloride.

or 1 molecule of hydrogen chloride is obtained from $\frac{1}{2}$ molecule of hydrogen and $\frac{1}{2}$ molecule of chlorine.

This is not against the atomic theory, since molecules are not indivisible. The molecule can be split up into its constituent atoms. The Avogadro's hypothesis was, therefore, adopted.

Avogadro's hypothesis was found to fit in with Gay Lussac's law in perfect harmony with Dalton's Atomic Theory.

Avogadro's hypothesis and Gay Lussac's law.—Like the laws of chemical combination by weight, Gay Lussac's law of gaseous volumes could not be explained by Dalton's atomic theory. The law was, however, clearly explained and interpreted on the basis of Avogadro's hypothesis from which it can be deduced as follows :

Let a molecules of a gas A react with b molecules of another gas B to form a compound of A and B—a and b are simple whole numbers. Let us further suppose that according to Avogadro's hypothesis 1 c.c. of each gas under the same conditions of temperature and pressure contain n molecules.

Then, a molecules of A are present in a/n c.c. of the gas A.
and b molecules of B are present in b/n c.c. of the gas B.

Hence, the reacting volumes of the two gases are a/n and b/n which bear the proportion $a : b$. This is a simple ratio, since both a and b are small whole numbers. Gases, therefore, react in simple ratio by volume, which is Gay Lussac's law.

---

* Also called Avogadro's law, since the hypothesis conforms to experimental tests of deductions made from it.

Avogadro's hypothesis and Dalton's Atomic Theory.—The adoption of Avogadro's hypothesis revolutionised our concept about the constitution of matter, and consequently substantially modified the atomic theory of Dalton. The modifications were mostly in the following lines : The concept of *simple atom* and *compound atom* was rejected—two kinds of smallest particle of matter recognised instead ; these are an *atom* and a *molecule.*

An atom, as stated already, is the smallest particle of an element which can take part in a chemical change ; the atom cannot usually exist as such in the *free state.*

A molecule, on the other hand, is the smallest particle of a substance (an element or a compound) which can exist in the *free state.* The properties of a substance are the properties of its molecules. Since atoms alone take part in a chemical change, prior to any chemical reaction, molecules of reacting substances first separate into atoms which then combine in simple numerical proportions to form molecules of new substances.

Application of Avogadro's hypothesis.—The hypothesis not only explained Gay Lussac's law of gaseous volumes, but also greatly extended the usefulness of Dalton's atomic theory by clearly explaining the confusion arising out of the concept of 'simple atom' and 'compound atom'.

The hypothesis is perfectly general in its applications, but it was only some fifty years later after its adoption that Cannizzaro, a pupil and a countryman of Avogadro, successfully applied it to experimental results in the year 1858. The hypothesis affords methods :

(i) *to determine the number of atoms in the molecule of a gaseous element,* i.e , *its atomicity.*
(ii) *to compare the molecular weights of gases and vapours and to deduce that the molecular weight of any gas or vapour is twice its vapour density.*
(iii) *to establish that the gram-molecular weight of any gas occupies 22.4 litres at N.T.P.*
(iv) *to deduce the molecular formula of a* gaseous *compound from its volumetric composition.*
(v) *to determine the atomic weight of an element.*

(i) To determine the number of atoms in the molecule of a gaseous element, i.e., its atomicity.

(a) Experiment shows that :

1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrogen chloride.

Let 1 volume of hydrogen contain *n* molecules of it, then, by Avogadro's hypothesis :

n molecules of hydrogen + *n* molecules of chlorine = 2*n* molecules of hydrogen chloride.

or 1 molecule of hydrogen + 1 molecule of chlorine = 2 molecules of hydrogen chloride.

or $\frac{1}{2}$ molecule of hydrogen + $\frac{1}{2}$ molecule of chlorine = 1 molecule of hydrogen chloride.

But according to Dalton's atomic theory, each molecule of hydrogen chloride, being a compound of hydrogen and chlorine, must contain *at least* one atom each of hydrogen and chlorine—coming from $\frac{1}{2}$ molecule each of hydrogen and chlorine. Hence, *a molecule of hydrogen or chlorine must contain at least* 2 *atoms, since atoms are indivisible.*

The exact number of atoms in a hydrogen molecule can be ascertained as follows :

(i) The number of different sodium salts that an acid can yield is a measure of its replaceable hydrogen atoms. Thus, sulphuric acid, H_2SO_4, yields two sodium salts, $NaHSO_4$, and Na_2SO_4, the two hydrogen atoms of the acid being replaceable in two stages. In a similar manner by replacing 3 hydrogen atoms of phosphoric acid, H_3PO_4, in three stages, three sodium salts, NaH_2PO_4, Na_2HPO_4 and Na_3PO_4 can be obtained. Hence the number of sodium salts that an acid forms is equal to its number of replaceable hydrogen atoms. Now hydrochloric acid yields only *one* sodium salt. The hydrochloric acid molecule, therefore, contains only one atom of hydrogen. But it has been shown to contain, as above, half a molecule of hydrogen. Half a molecule of the gas, therefore, contains one atom of hydrogen. Hence a molecule of hydrogen contains two atoms, or in other words, *the hydrogen molecule is diatomic,* i.e., *the atomicity of hydrogen is two.*

(ii) The ratio of the specific heat of a gas at constant pressure, Cp, and that at constant volume, Cv, has been found to be equal to 1.44, *i.e.*, $Cp/Cv = 1.44$, for diatomic gases. In the case of hydrogen this ratio is found to be 1.44 and hence the gas is diatomic.

(b) 2 vols. of hydrogen + 1 vol. of oxygen = 2 vols. of steam.

Let 1 volume hydrogen contain *n* molecules of it, then by Avogadro's hypothesis :

2 molecules of hydrogen + 1 molecule of oxygen = 2 molecules of steam.

or 1 molecule of hydrogen + $\frac{1}{2}$ molecule of oxygen = 1 molecule of steam.

But 1 molecule of steam must contain *at least* one atom of oxygen, coming from $\frac{1}{2}$ molecule of oxygen. Hence a molecle of oxygen is *at least diatomic.*

The *atomicity*, i.e., the number of atoms in a molecule of elementary gases like hydrogen, oxygen, nitrogen, chlorine, etc., is *two* only.

(ii) **The molecular weight of any gas or vapour is twice its vapour density.**

The density of a gas or vapour relative to hydrogen is the ratio of the weight of a volume of the gas or vapour to the weight of the same volume of hydrogen under the same conditions of temperature and pressure.

By definition, *relative density* or *vapour density*, as it is called.

$$= \frac{\text{weight of a certain volume of the gas or vapour}}{\text{weight of the } \textit{same} \text{ volume of hydrogen}}$$

at the same temperature and pressure. But equal volumes of the gas and hydrogen contain the same number of molecules, Avogadro's hypothesis. Hence,

$$\text{vapour density} = \frac{\text{weight of } n \text{ molecules of gas or vapour}}{\text{weight of } n \text{ molecules of hydrogen}} = \frac{\text{weight of 1 molecule of gas or vapour}}{\text{weight of 1 molecule of hydrogen}}$$

$$= \frac{\text{molecular weight of gas or vapour}}{\text{molecular weight of hydrogen}} = \frac{\text{mol. wt. of gas or vapour}}{2}$$

since a molecule of hydrogen is diatomic and its atomic weight is one

$\therefore$ *molecular weight of gas* or *vapour* = 2 × *its vapour density.*

Actually the atomic weight of hydrogen is 1.008 and its molecular weight is 2.016 instead of 2, so that

molecular weight = *vapour density* × 2.016.

(iii) **Gram-molecular weight of gas or vapour occupies 22.4 litres at N.T.P.**

Molecular weight of gas or vapour expressed in grams is its gram molecular weight. One litre of hydrogen at N.T.P. weighs 0.09 gm. nearly.

$$\text{Vapour density} = \frac{\text{weight of 1 litre of gas or vapour at N.T.P.}}{\text{weight of 1 litre of hydrogen at N.T.P.}} = \frac{\text{weight of 1 litre of the gas at N.T.P.}}{0.09}$$

$\therefore$ weight of 1 litre of gas or vapour at N.T.P.

= 0.09 × its vapour density = 0.09 × (M/2.016),

where M = gram-molecular weight of the gas.

i.e., 0.09 × (M/2.016) gm. of gas or vapour occupy a volume of 1 litre at N.T.P.

$\therefore$ M gm. of gas or vapour occupy (2.016/0.09) or 22.4 litres at N.T.P.

Hence, the gram-molecular weight of *any* gas or vapour occupies 22.4 litres at N.T.P. This is called the *gram-molecular volume or molar volume.*

(iv) **Molecular formula of a compound from its volumetric composition.**

Erperiments show that : 2 volumes of steam are obtained from 2 volumes of hydrogen and 1 volume of oxygen.

Suppose 1 volume of steam contains n molecules of it, then, by Avogadro's hypothesis, $2n$ molecules of steam are obtained from $2n$ molecules of hydrogen and n molecules of oxygen.

2 molecules of steam are obtained from 2 molecules of hydrogen and 1 molecule of oxygen.

∴ 1 molecule of steam is obtained from 1 molecule of hydrogen and half molecule of oxygen.

Now, 1 molecule of hydrogen contains 2 atoms of hydrogen ; half-molecule of oxygen contains 1 atom of oxygen.

∴ the simple formula for steam is H_2O.

Again, the molecular weight of steam $= 2 \times 9 = 18$; 9 is the vapour density of steam determined experimentally.

Hence, the formula H_2O for steam is confirmed, since 1 molecule of steam can contain only 1 atom of oxygen, its atomic weight being 16.

(v) **Atomic weight of an element.**—(a) **From the atomicity of elementary gases :**

Atomic weight = molecular weight ÷ atomicity.

Molecular weight is deduced from the determination of vapour density. The molecular weight of the element argon, for example, is found to be 39.9 and its atomicity is 1. Hence the atomic weight of argon is 39.9.

(b) **Cannizzaro's method of least weight.**—Since an atom is indivisible, no molecule of a compound can contain less than one atom of any element. Hence, *the atomic weight of an element may be defined as the smallest weight of it found in the molecular weight of any of its compounds.*

The method depends upon the determination of :

(i) the molecular weights of a large number of **volatile** compounds (deduced from the relation molecular weight = 2 × its vapour density, vapour density being determined experimentally).

(ii) their percentage compositions by direct analysis. The weight of the element present in the molecular weight of each compound is then calculated—the least of these weights is the *probable* atomic weight of the element.

The method is obviously applicable in the case of elements which form a large number of *volatile* compounds.

The application of the method to nitrogen is illustrated below.

Compound	Mol. wt.	% N_2 by wt.	Wt. of N_2 per mol.
Ammonia	17	82.3	$17 \times 0.823 = 14$
Nitrous oxide	44	63.6	$44 \times 0.636 = 28$
Nitric oxide	30	46.6	$30 \times 0.466 = 14$
Dinitrogen tetroxide	92	30.4	$92 \times 0.304 = 28$

Hence, the *probable* atomic weight of nitrogen is 14, since it is the least weight of nitrogen found in any of its compounds.

Molecular weights determined from vapour densities of the compounds are not exact, and consequently the atomic weights found by Cannizzaro's method are only approximate.

✓**Avogadro Number and Molar Volume.**—In fixing the relative atomic weights the atomic weight of hydrogen has been taken as 1, and since hydrogen is *diatomic* its molecular weight is 2—weight of 1 gram molecule of hydrogen is 2 gms. Suppose the *absolute weight* of an atom of hydrogen is w gm., and hence the weight of 1 molecule of hydrogen is $2w$ gm. ∴ the number molecules in 1 gram molecular weight of hydrogen $= 2/2w = 1/w$.

Taking the case of oxygen, its vapour density is 16 and hence the molecular weight = 2 × 16 = 32. In other words, a molecule of oxygen is 32 times as heavy as an atom of hydrogen. Hence the weight of 1 molecule of oxygen = 32 w gm. ∴ number of molecules in 1 gram molecular weight of oxygen = 32/32w = 1/w. Considering carbon dioxide whose vapour density is 22 and hence the molecular weight 44, 1 molecule of carbon dioxide is 44 times as heavy as an atom of hydrogen. Hence the weight of 1 molecule of carbon dioxide = 44w gm.

∴ number of molecules in 1 gram molecular weight of carbon dioxide
= 44/44w = 1/w.

It is evident from the above that 1 gram molecular weight of any gas contain the same number of molecules—this number is known as **Avogadro number,** usually denoted by N and is equal to 6.023×10^{23}.

Now, since 1 gram molecule of any gas contains the same number of molecules, from Avogadro's hypothesis 1 gram molecule of any gas will occupy the *same* volume under the same conditions of temperature and pressure. It has been found experimentally that 1 gram molecular weight, i.e., 2 gm., of hydrogen occupy 22.4 litres at N.T.P. Hence 1 gram molecule of any gas will occupy 22.4 litres at N.T.P. This is called **molar volume.**

Exercises

1. A metal is found to give two oxides ; on heating 1 gm. of each in a current of hydrogen, 0.798 and 0.888 gms. of the metal were obtained. Show that the results are in agreement with the law of multiple proportion.

In the first oxide (1−0.798) or 0.202 gm. of oxygen unite with 0.798 gm. of the metal.

∴ 1 gm. of oxygen unites with 0.798/0.202 or 3.95 gms. of the metal.

In the second oxide (1−0.888) or 0.112 gm. of oxygen unites with 0.888 gm. of the metal.

∴ 1 gm. of oxygen unites with 0.888/0.112 or 7.9 gm. of the metal.

Hence the weights of the metal uniting with a constant weight, namely, 1 gm. of oxygen, are as 3.95 to 7.9, that is, as 1 : 2. Hence the agreement.

2. Illustrate the law of reciprocal proportions from the composition of the following compounds :

Marsh gas 75% carbon, 25% hydrogen ; carbon monoxide 42.86% carbon, 57.14% oxygen ; and water 11.11% hydrogen, 88.89% oxygen.

In marsh gas 1 gm. of carbon unites with 25/75 or 0.33 gm. of hydrogen.

In carbon monoxide 1 gm. of carbon unites with 57.14/42.86 or 1.33 gm. of oxygen.

Hence, hydrogen and oxygen should unite in the ratio of 0.33 to 1.33, i.e., in the ratio of 1 to 4 ; or in some simple multiples thereof.

In water 11.11 gm. of hydrogen united with 88.89 gm. of oxygen.

∴ 1 gm. of hydrogen unites with 88.89/11.11 or 8 gms. of oxygen.

i.e., hydrogen and oxygen unite to form water in the ratio of 1 to 8 parts by weight, that is, in the ratio of 1 to 2×4 parts by weight.

Hence these figures agree with the law of reciprocal proportions.

③ Two oxides of a metal M, when heated to a constant weight in a current of hydrogen gave 0.12585 g. and 0.2264 g. of water respectively per gram of the oxides used. If the formula for the latter be given by MO, find that for the other.

18 gms. of water H_2O contain 16 gms. of oxygen.

0.12585 g. of water contains $\frac{16}{18} \times 0.12585 = 0.1119$ gm. of oxygen.

This 0.1119 g. of O_2 comes from 1 gm. of first oxide, and hence in 1 gm. of first oxide, M = 0.8881 gm., and O = 0.1119 gm.

0.2264 gm. of water contain $\frac{16}{18} \times 0.2264 = 0.2013$ gm. of oxygen.

$\therefore$ in 1 gm. of second oxide, M = 0.7987 gm., and O = 0.2013 gm.

Now, formula of the second oxide is MO, i.e.,

$$\frac{\text{Number of atoms of M}}{\text{Number of atoms of O}} = \frac{1}{1} = \frac{0.7987/x,}{0.2013/16,}$$

where x = atomic weight of M, and 16 = atomic weight of oxygen.

$$\therefore \quad x = \frac{0.7987}{0.2013} \times 16 = 63.49.$$

In the first oxide, $\frac{\text{number of atoms of M}}{\text{number of atoms of O}} = \frac{0.8881/63.49}{0.1119/16} = \frac{2}{1}$

$\therefore$ formula of first oxide is M_2O.

---

4. State and explain the laws of chemical combination. Give some account of experimental evidence upon which they are based.

Two oxides *a* and *b* of a certain metal were heated to constant weight in a current of hydrogen and the water obtained in each case was weighed. The following results were obtained : 2 gm. of *a* gave 0.2517 gm. of water, and 1 gm. of *b* gave 0.2264 gm. of water. Show that the above results illustrate the law of multiple proportion.

5. Illustrate the law of equivalent proportion from the following analysis :

Potassium chloride	potassium	52.5% ;	chlorine	47.5%.
Potassium iodide	potassium	23.6% ;	iodine	76.4%.
Chloride of iodine	iodine	78.2% ;	chlorine	21.8%.

6. What is Avogadro's hypothesis ? Explain, with illustrations, how this hypothesis brings into harmony Dalton's atomic theory and Gay Lussac's law of combining volumes. State how it is used to prove that (i) the atomicity of oxygen is two ; (ii) the molecular weight of any gas is twice its vapour density, and (iii) the gram molecular weight of any gas is 22.4 litres at N.T.P.

7. State and explain Gay Lussac's Law of combining volumes. Four compounds of an element contain respectively 42.8%, 27.3%, 80%, and 64.90% of the element. The weights of one litre of each of these compounds in a gaseous state at N.T.P. are 1.26 gms, 1.98 gms., 1.35 gms. and 3.33 gms. respectively. Calculate the probable atomic weight of the element and explain the principle involved in the determination of atomic weights by Cannizzaro's method. *Ans.* 12

8. State how the results given below illustrate a law of chemical action. Enunciate the law.

(a) 0.46 gm. of magnesium produce 0.77 gm. of magnesium oxide.
(b) 0.82 gm. of magnesium liberates 760 c.c. of hydrogen at N.T.P. from an acid.
(c) 1.26 gm. of water result from the union of 1.12 gm. of oxygen with hydrogen.

9. State and illustrate the law of multiple proportion. Does it contradict the law of constant proportion ? Three oxides of lead have the following composition :

	(i)	(ii)	(iii)
Lead	92.85	90.63	86.51 per cent.
Oxygen	7.15	9.37	13.49 per cent.

Show how these figures bear out the law of multiple proportion.

10. State Dalton's Atomic Theory and show how the laws of chemical combination can be deduced from it. *Inter Science, London.*

11. The percentage composition of ferrous sulphide is : iron 63.53 per cent, sulphur 36.47 per cent. Two grams of iron are heated with 5 gms. of sulphur. How much ferrous sulphide is formed and how much sulphur remains uncombined ? *Ans.* 3.148 gms ; 3.852 gms.

12. Explain and illustrate Gay Lussac's law of gaseous volumes and show how it has led to the distinction between atoms and molecules.

13. State and illustrate the law of multiple proportions. Explain how it follows directly from Dalton's atomic theory. *Gauhati, 1952*

Two oxides of a metal contain 27.6 and 30.0 per cent of oxygen respectively. If the formula of the first be M_3O_4, find that of the second. *Ans.* M_2O_3

14. Enunciate Avogadro's hypothesis and show how it leads to a clear interpretation of Gay-Lussac's law of gaseous volumes. Discuss how the Avogadro's hypothesis has proved useful in the determination of atomic weight of gaseous elements. *Calcutta, 1959*

15. Enunciate Avogadro's hypothesis, and mention its important applications. *U. P. Board, 1950*

VIII

CHEMICAL EQUIVALENTS AND ATOMIC WEIGHTS

An important consequence of the law of reciprocal proportions is the emergence of the idea of equivalent weight ; thus

In *sodium hydride*, NaH, the ratio by weight of hydrogen to sodium is 1 : 23.

In *hydrogen chloride*, HCl, the ratio by weight of hydrogen to chlorine is 1 : 35.457.

The law of reciprocal proportions suggests that sodium and chlorine will combine in the proportion of 23 : 35.457 or in a simple multiple of this proportion. Thus, 23 parts by weight of sodium combine with 35.457 parts by weight of chlorine to form sodium chloride. 23 and 35.457 are the *equivalent weights* of sodium and chlorine respectively. Hence :

Elements combine in the ratio of their equivalent weights or their multiples.

Standard of Equivalents.—In finding out the equivalent weight of an element it is necessary to fix upon a standard of reference—this is taken as 8 parts by weight of oxygen i.e., *equivalent weight of oxygen is always* 8.000 *by definition.*

Formerly 1 part by weight of hydrogen was the standard, but since there are many elements. particularly metals, which do not form stable compounds with hydrogen, the basis of definition was changed to oxygen. But there are some elements which do not form stable compounds with oxygen. In order, therefore, to maintain the oxygen standard, the standard of reference is extended to *equivalents of oxygen.* On the basis of 8.000 as the equivalent weight of oxygen, the equivalent weight of hydrogen is 1.008, that of carbon (in CO_2) is 3.0025, and that of chlorine (in Cl_2O) is 35.457.

Hydrogen was taken as the standard by Dalton but the adoption of oxygen as the standard was due mainly to Berzelius and Stas.

Equivalent weight.—*The equivalent weight of an element is defined as the number of parts by weight of that element which will combine chemically with or will replace from chemical combination,* 8.000 *parts by weight of oxygen, or its equivalent, i.e.,* 1.008 *parts by weight of hydrogen or* 35.457 *parts by weight of chlorine.*

The equivalent weight is a *number ; the gram equivalent is the equivalent weight expressed in grams.* The equivalent weight is an experimental quantity.

Illustrations.—(i) 1.008 parts by weight of hydrogen combine with 8 parts by weight of oxygen to form water, H_2O ; the equivalent weight of hydrogen, therefore, is 1.008.

(ii) 1.008 parts by weight of hydrogen combine with 35.457 parts by weight of chlorine to form hydrogen chloride ; consequently the equivalent weight of chlorine is 35.457.

(iii) 35.457 parts by weight of chlorine combine with 107.88 parts by weight of silver ; equivalent weight of silver is, therefore, 107.88.

(iv) 12.16 parts by weight of magnesium displace 1.008 parts by weight of hydrogen from dilute sulphuric acid. 12.16 is the equivalent weight of magnesium :

$$Mg + H_2SO_4 = MgSO_4 + H_2.$$

Equivalent weight may vary.—Equivalent weight of an element is determined by direct analysis of its compounds. When it forms more than one compound with another element, its equivalent naturally varies. Thus, iron forms two oxides : ferrous oxide, FeO ; ferric oxide, Fe_2O_3.

Compound	Composition by weight	Equivalent
Ferrous oxide	Fe : O = 27.925 : 8	Fe = 27.925
Ferric oxide	Fe : O = 18.616 : 8	Fe = 18.616
Carbon dioxide	C : O = 3.00 : 8	C = 3.00
Carbon monoxide	C : O = 6.00 : 8	C = 6.00

It also follows from the relation : *atomic weight = equivalent weight × valency that equivalent weight may vary* in the case of elements of *variable valency*, since atomic weight is a constant quantity.

Equivalent of a Radical.—The concept of equivalent of an element is extended to radicals, i.e., the equivalent of a radical is the number of parts by weight of it which can combine with 1.008 parts by weight of hydrogen or its equivalent.

Compound	Composition by weight	Equivalent of radical
HNO_3	$H : NO_3 = 1 : 62$	$NO_3 = 62$
H_2SO_4	$H : SO_4 = 1 : 48$	$SO_4 = 48$
NH_4Cl	$NH_4 : Cl = 18 : 35.457$	$NH_4 = 18$

The equivalent weight of an element is a fundamental value, and the equivalent weight of a compound is formed additively from those of its constituent elements (or radicals). The equivalent weight of silver chloride = equivalent weight of silver + equivalent weight of chlorine = 107.88 + 35.457 = 143.337.

Equivalent of element or radical	Equivalent of compound
Ca—20 ; Cl—35.457	Calcium chloride 55.457
Mg—12.16 ; O—8.00	Magnesium oxide 20.16
Ag—107.88 ; NO_3—62	Silver nitrate 169.88

Determination of equivalent weights of metals.—(i) **By displacing hydrogen from an acid by a given weight of the metal.**

When a metal displaces hydrogen from an acid, the displacement takes place in equivalent amounts. The hydrogen liberated is collected, its volume measured in c.c. and reduced to N.T.P., and its weight calculated from the ralation :

Weight of hydrogen = c.c.'s of hydrogen at N.T.P. × 0.00009 gm., since weight of 1 c.c. of hydrogen at N.T.P. = 0.00009 gm.

$$\text{Equivalent weight of the metal} = \frac{\text{Weight of the metal} \times 1.008.}{\text{Weight of hydrogen liberated.}}$$

The method is limited in its applicability to metals which dissolve in dilute acids (or alkali) with evolution of hydrogen. *Calcium, magnesium, zinc and iron* dissolve in cold dilute HCl or H_2SO_4, evolving hydrogen. Aluminium dissolves in fairly strong HCl or warm alkali, while tin dissolves only in hot and strong hydrochloric acid. The method has been used to determine equivalents of *zinc* and *aluminium*.

Equivalent weight of zinc.—About 0.1 gm. of zinc is accurately weighed out in a watch glass, which is then placed in a beaker—the zinc being covered with a funnel. Water is then added till the stem of the funnel is under water. A graduated tube completely filled with water is inverted over the funnel and fairly strong sulphuric acid is added to the beaker. Quick evolution of hydrogen takes place on the addition of few drops of copper sulphate solution—the gas collects in the tube. When the zinc completely dissolves, the tube is taken out by closing the open end with the thumb, and placed in a jar of water so that the level of water inside and outside becomes the same. The volume of hydrogen is noted, so also the barometric pressure at the time and the temperature of water. (fig. 38).

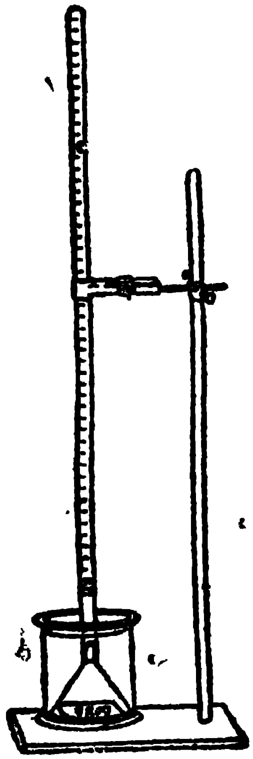


Fig. 38

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

Calculation :

Let the weight of zinc = w gm.
Volume of hydrogen collected = v c.c.
Temperature of water = t°C.
Barometric pressure = P mm.
Aqueous tension at t°C = f mm.

Barometric pressure = pressure of H_2 + aqueous tension at t°C.

$\therefore$ Pressure of H_2 = (P−f) mm.

Let the volume of the hydrogen at N.T.P. be v′ c.c.

$$\therefore \frac{v(P-f)}{(273+t)} = \frac{v'.760}{273} \text{ or } v' = \frac{v \times (P-f) \times 273}{(273+t) \times 760} \text{ c.c.}$$

Now, 1 c.c. of hydrogen at N.T.P. weighs 0.00009 gm. nearly.

$\therefore$ v′ c.cs. of hydrogen at N.T.P. weighs $v' \times 0.00009$ gm.

$$\therefore \text{ equivalent of zinc} = \frac{w \times 1.008}{v' \times 0.00009} = \frac{w \times (273+t) \times 760 \times 1.008}{v \times (P-f) \times 273 \times 0.00009}$$

(ii) By converting a known weight of the metal into its oxide, and weighing the oxide.

Suppose— gm.
the weight of the metal w
the weight of the oxide w′
$\therefore$ the weight of oxygen (w′−w)

$$\therefore \text{ the equivalent weight of the metal} = \frac{w}{(w'-w)} \times 8.$$

The equivalent weight of oxygen is 8 by definition.

(a) by heating metal in air : Equivalent weight of magnesium :

A porcelain crucible and its lid are weighed. A piece of clean magnesium ribbon about 5 inches long is broken into pieces and taken in the crucible, which is then weighed again with its lid. The crucible is then slowly heated on a clay-pipe triangle, with its lid put slightly on one side in order that air might have access to magnesium. When the magnesium is burnt completely, the crucible is cooled in a desiccator, and weighed again. $2Mg + O_2 = 2MgO$.

Calculation :

	gm.
Weight of crucible + lid	a
Weight of crucible + lid + magnesium	b
Weight of crucible + lid + magnesium oxide	c
∴ weight of magnesium	(b − a)
Weight of magnesium oxide	(c − a)
∴ weight of oxygen	(c − b)

$$\therefore \text{ equivalent weight of magnesium} = \frac{(b-a)}{(c-b)} \times 8.$$

(b) by converting the metal into the nitrate by allowing nitric acid to act on the metal—the nitrate decomposes, on strong heating, into the oxide.

Equivalent weight of copper.—A porcelain crucible with its lid is weighed. A few pieces of clean copper foil, about 2 gm., are put into the crucible, which is again weighed with its lid. Few drops of moderately strong nitric acid are added to the copper foils in the crucible—a vigorious reaction takes place with the evolution of brown fumes. When the copper has dissolved fully, the solution is carefully evaporated to dryness on a hot asbestos plate so that none of the green copper nitrate is lost by spirting. The crucible with its lid placed slightly on its side is then heated on a clay-pipe triangle where the green copper nitrate is converted into the black copper oxide, and more brown fumes are evolved. When the reaction has ceased, the crucible with its lid is allowed to cool in a desiccator and weighed again. The process of heating, cooling and weighing is repeated till the final weight is constant. The weight of copper combining with 8 gm. of oxygen is found out by proportion.

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2$$

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

Taking the same figures as in the equivalent weight of magnesium, the equivalent weight of copper $= \frac{(b-a)}{(c-b)} \times 8$.

The method has been applied in finding the equivalents of *copper, tin, zinc* and *iron.*

Tin reacts with strong nitric acid to give hydrated stannic oxide directly without the formation of any nitrate at all.

(iii) By reduction of a given weight of the oxide of a metal to the metal : $CuO + H_2 = Cu + H_2O$.

Many metallic oxides are reduced to the metal by hydrogen or coal gas. The method is illustrated with copper oxide. A porcelain boat is weighed empty, and then containing some dry black oxide of copper. The boat is then slipped into a hard glass tube and heated in a current of hydrogen gas, when the oxide is reduced to the metal. After about half an hour, the tube is cooled with the current of gas still on. When cold the boat with the reduced copper is taken out and weighed (fig. 36).

Calculation :

	gm.
Weight of boat	a
Weight of boat + copper oxide	b
Weight of boat + copper	c
∴ weight of copper	(c−a)
weight of oxygen	(b−c)

$$\therefore \text{ the equivalent weight of copper} = \frac{(c-a)}{(b-c)} \times 8.$$

(iv) **By the analysis of halides.—Equivalent weight of sodium.**—A weighed quantity of pure sodium chloride is dissolved in distilled water containing a little nitric acid, and precipitated as silver chloride by adding an excess of silver nitrate solution. The curdy white precipitate of the silver chloride is filtered, washed, dried and weighed. The reaction is : $NaCl + AgNO_3 = AgCl + NaNO_3$.

One equivalent of sodium chloride produces one equivalent of silver chloride. Hence the equivalent weight of sodium chloride is the weight which produces 143.34 gm. of silver chloride. 143.34 gm. is equal to 1 gram-equivalent of silver chloride, i.e., 107.88 gm. of of silver react with 35.46 gm. of chlorine to form (107.88+35.46) = 143.34 gm. of AgCl.

The equivalent of sodium is 35.457 less than the equivalent of sodium chloride, since sodium and chlorine have combined in equivalent amounts.

Calculation.—Let the weight of sodium chloride = w gms.
The weight of silver chloride = w′ gms.

w′ gms. of AgCl are produced by w gm. of the sodium chloride.

∴ 143.34 gms. of AgCl are produced by 143.34 w/w′ gm. sodium chloride.

i.e., equivalent of sodium chloride = 143.34 w/w′.

∴ the equivalent weight of sodium = (143.34 w/w′)−35.457.

Alternatively, let the equivalent of sodium = x.

∴ the equivalent of sodium chloride = x + 35.457.

$$\frac{\text{Equivalent of sodium chloride}}{\text{Equivalent of silver chloride}} = \frac{\text{weight of sodium chloride}}{\text{weight of silver chloride}}$$

i.e., $(x+35.457)/143.34 = w/w'$, ∴ $x = (143.34\, w/w') - 35.357$.

The method has been used in determining the equivalents of *sodium, potassium, calcium, magnesium, zinc* (using the bromide), *lead, arsenic, silicon, iron* (using the bromide), and *nitrogen* (as NH_4Cl).

(v) **By the replacement of metals.**—A more electropositive metal displaces a less electropositive metal from its salts in solution—the displacement taking place in equivalent amounts. The method is applicable when a metal displaces another from a solution. Thus, if a piece of iron, (say, a knife-blade) is put into copper sulphate solution, it becomes coated with a red deposit of copper, and the iron dissolves :

$$CuSO_4 + Fe = FeSO_4 + Cu.$$

Illustration.—A known weight of clean iron powder is gradually added into a solution of copper sulphate in a beaker ; the iron dissolves and red copper powder deposits at the bottom of the beaker. It is filtered off, and washed with water until the wash-water is no longer coloured blue. The filter paper with its contents is then dried in an air-oven, and weighed. Then, knowing the equivalent of one metal, that of the other may be found out.

Let w gm. of iron displace w′ gm. of copper.

∴ 1 gm. of iron displaces w′/w gm. of copper.

Let the eq. wt. of iron = x, and eq. wt. of copper = y.

∴ x gm. of iron can displace y gm. of copper.

∴ 1 gm. of iron can displace y/x gm. of copper.

$$\therefore \frac{y}{x} = \frac{w'}{w} \text{ i.e., } \frac{\text{eq. wt. of Cu}}{\text{eq. wt. of Fe}} = \frac{\text{wt. of Cu deposited}}{\text{wt. of Fe dissolved}}$$

Knowing the equivalent of copper, that of iron can be found out, or *vice versa.* Copper in its turn, displaces silver from a solution of its salt.

$$2AgNO_3 + Cu = Cu(NO_3)_2 + 2Ag.$$

(vi) **By interchange of radicals.**—When a compound of a metal, *say* MA, is quantitatively converted into another compound, *say* MB, then the equivalent of any of the three radicals involved can be found out, provided the equivalents of the other two radicals are known. The method is explained with reference to the *equivalent weight of barium* :—

A weighed quantity of barium chloride is dissolved in distilled water containing a little hydrochloric acid, and precipitated as barium sulphate by adding an excess of sulphuric acid—the precipitate is filtered, washed, dried and weighed.

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

Let the weight of barium chloride = w_1 gm.

The weight of barium sulphate = w_2 gm.

i.e., w_1 gm. of barium chloride gives w_2 gm. of $BaSO_4$

∴ 1 gm. of barium chloride gives w_2/w_1 gm. $BaSO_4$.

Let the equivalent weight of barium = x

The equivalent weight of chlorine = 35.457

The equivalent weight of sulphate = 48

Hence, the equivalent weight of barium chloride = x + 35.457 and the equivalent weight of barium sulphate = x + 48.

Now 1 equivalent of barium chloride gives 1 equivalent of barium sulphate.

i.e., (x+35.457) gm. of barium chloride gives (x+48) gm. of barium sulphate.

$$\therefore \ 1 \text{ gm. of barium chloride gives } \frac{x+48}{x+35.457} \text{ gm. of barium sulphate ;}$$

$$\text{Hence, } \frac{x+48}{x+35.457} = \frac{w_2}{w_1} \text{ whence x is found out.}$$

(vii) **From electro-chemical equivalents.**—The equivalent weight may be determined from the relation (*vide electrolysis*) :

$$\text{equivalent weight} = \frac{\text{electro-chemical equivalent}}{0.0000104} \times 1.008.$$

Equivalents of silver and chlorine.—A weighed quantity of pure silver is dissolved in fairly strong nitric acid to get the nitrate of the metal. The silver is precipitated from the solution as curdy white silver chloride by adding an excess of hydrochloric acid. The precipitate is filtered, washed, dried, and weighed.

Let the weight of silver = a gm.
the weight of silver chloride = b gm.

Let the eq. wt. of silver = x, and the eq. wt. of chlorine = y.

∴ eq. wt. of silver chloride = $x + y$.

1 equivalent of Ag produces 1 equivalent of silver chloride.

$$\frac{\text{wt. of silver}}{\text{wt. of silver chloride}} = \frac{\text{equivalent of silver}}{\text{equivalent of silver chloride.}} \text{ or } \frac{a}{b} = \frac{x}{x+y}$$

Knowing the equivalent of silver, that of chlorine can be found out, or *vice versa*.

The equivalent weight of chlorine may also be determined :

(i) by burning weighed quantities of hydrogen and chlorine, and measuring the quantity of hydrogen chloride produced. The weight of chlorine combining with 1.008 parts by weight of hydrogen is the equivalent of chlorine.

(ii) by accurately determining the molecular weight of hydrogen chloride which contains one atom each of hydrogen and chlorine.

The molecular weight of HCl was found to be 36.466 ; hence the equivalent of chlorine = 36.466 − 1.008 = 35.458.

(iii) by displacing the hydrogen in hydrogen chloride with aluminium. Let v litres of hydrogen chloride at N.T.P. yield v' litres of hydrogen at N.T.P. Let their densities be d and d' respectively. Hence the weights of hydrogen chloride and hydrogen are vd and $v'd'$ respectively. Then, the equivalent of chlorine $= \frac{vd - v'd'}{v'd'} \times 1.008$. Gray and Burt (1909) found the equivalent to be 35.458.

The accepted value is 35.457.

The equivalent weight of hydrogen.—The accepted value is 1.008 with reference to the equivalent weight of oxygen which is 8.0000 by definition. The most exact determination of the equivalent of hydrogen was made by Morley in 1895 in the following way :

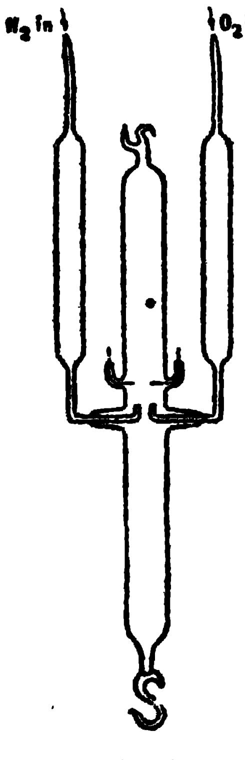


Fig. 39

Pure and dry hydrogen and oxygen were weighed in large glass globes. In later experiments the hydrogen was weighed, absorbed in palladium and driven out pure by heating. Sufficient quantities of hydrogen and oxygen (to produce about 34 grams of water) were made to stream in the ratio of 2 : 1 into a previously weighed evacuated glass vessel (fig. 39) and burnt therein at platinum jets to produce water. The weights of H_2 and O_2, admitted to the apparatus, were obtained from the decrease in weight of the globes. During the burning the vessel was immersed in cold water. The water produced was then frozen and the residual gas pumped out of the vessel through a tube containing phosphorus pentoxide (to keep back water vapour) and analysed. The weights of unreacted hydrogen and oxygen found were subtracted from the weights of the two gases supplied from the weighed globes and the weights of H_2 and O_2, actually burnt to water, found out. After the removal of residual gas, the apparatus was weighed—the increase in weight gives the weight of water formed. From the weights of oxygen, hydrogen, and water formed, Morely found the ratio of oxygen to hydrogen as 8 to 1.0076. Morely determined the composition of water *by weight*.

Let wt. of H_2 admitted = *a* g. ; wt. of O_2 admitted = *b* g.
wt. of residual H_2 = *c* g. ; wt. of residual O_2 = *d* g.
∴ wt. of H_2 burnt = (a−c) g. ; wt. of O_2 burnt = (b−d) g.
∴ in water, wt. of H_2/wt. of O_2 = (a−c)/(b−d) = 1.0076 : 8.

Equivalent weight of carbon.—The equivalent of carbon is determined by burning a weighed amount of pure sugar charcoal taken in a tared porcelain boat in a stream of oxygen, and absorbing the carbon dioxide formed in weighed potash bulbs. For details see gravimetric composition of carbon dioxide.

Calculation : Wt. of porcelain boat = a gm.
wt. of boat + charcoal = b gm.
∴ wt. of charcoal = (b−a) gm.
wt. of potash bulb before expt. = c gm.
wt. of potash bulb after expt. = d gm.
∴ wt. of CO_2 formed = (d−c) gm.
Let the equivalent of carbon = x
∴ equivalent of carbon dioxide = x + 8

$$\therefore \frac{\text{Equivalent of CO}_2}{\text{Equivalent of C}} = \frac{\text{weight of CO}_2\text{ formed}}{\text{weight of carbon}}$$

$$\text{i.e. } \frac{x+8}{x} = \frac{d-c}{b-a} \qquad \therefore\ x = \frac{(b-a)\times 8}{(d-c)-(b-a)}$$

Atomic weight.—Each kind of atom has a definite *weight*. But it is difficult to determine the absolute weight of an atom of the element (p. 22). It has been convenient in practice to state the relative weight of any atom in terms of that of a standard atom.

Formerly the atom of the lightest element hydrogen was chosen (by Dalton) as the standard of comparison and its atomic weight was taken as unity. But now the standard of comparison is oxygen.

Since atomic weight is generally determined from the equivalent weight, 16.00 is taken as the atomic weight of oxygen.

The atomic weight of an element is the weight of an atom of the element relative to the weight of the oxygen atom taken as 16.0000. On this basis, the atomic weight of hydrogen is 1.008.

The *gram-atomic weight* or the *gram-atom* of an element is its atomic weight expressed in grams : thus 16 grams of oxygen constitute one gram atom of oxygen.

Relation between atomic weight and equivalent weight :—

Let the atomic weight of the element $= a$,
equivalent weight of the element $= e$,
valency of the element $= v$,

then, by definition of valency :
v atoms of hydrogen combine with 1 atom of the element,
or, *v* parts by weight of hydrogen combine with *a* parts by weight of the element,
or 1 part by weight of hydrogen combines with *a*/*v* parts by weight of the element.

Hence, by definition of equivalent weight, $a/v = e$, or $a = e \times v$.
i.e., ***atomic weight = equivalent weight × valency.***

Determination of atomic weights.—The exact atomic weight of an element is determined from the relation :

atomic weight = equivalent weight × valency.

The atomic weight of an element is, therefore, either the same as the equivalent weight when the valency is 1, or an exact multiple of the equivalent weight, since the valency is always a small integer.

The determination of atomic weight resolves into two parts :

(a) *the determination of the equivalent weight.* This may be accurately found out by chemical analysis.

(b) *the determination of the valency of the element.* The valency is usually determined by dividing the approximate atomic weight (which may be found out in several ways, as mentioned below) by the equivalent weight and taking the nearest integer as a correct number, since the valency is always a whole number.

The approximate atomic weight may be found out in several ways :

(i) **By Dulong and Petit's law** :—The atomic heat of a solid element (except *carbon, silicon, boron, and beryllium*) is approximately constant at ordinary temperature, and is equal to 6.3 nearly. Dulong and Petit put forward the above law in 1819.

The product of the atomic weight and specific heat of an element is known as atomic heat, and consequently,

atomic weight × specific heat = 6.3 approximately.

The law is *approximate* and applies to *solid* elements only.

In order to determine the *exact* atomic weight find out :

(a) approximate atomic weight from the realition :
approximate at. wt. = 6.3/sp. ht. ;

(b) then valency from : valency = approximate at. wt./eq. wt.
The value of valency, thus obtained, is corrected to the nearest integer, since valency is always a whole number.

(c) *finally,* apply the relation exact atomic weight = equivalent weight × valency.

Example.—0.5574 *gm. of a metal was converted into* 0.6817 *gm. of oxide. The specific heat of the metal is* 0.063. *Find the exact atomic weight.*

$$\text{The equivalent of metal} = \frac{0.5574}{0.1243} \times 8 = 35.88$$

By Dulong and Petit's law, atomic weight × specific heat = 6.3 nearly

$\therefore$ rough atomic weight = 6.3/0.063 = 100.

$$\therefore \text{ valency} = \frac{\text{rough atomic weight}}{\text{equivalent weight}} = \frac{100}{35.88} = 2.8.$$

Hence valency = 3, since the valency is always an integer.

$\therefore$ exact atomic weight = 35.88 × 3 = 107.64.

(ii) **By Cannizzaro's method** :—*From molecular weights of volatile compounds.*—The method gives the *probable* atomic weight. The weight is approximate only. (See page 87).

(iii) **By finding the vapour density** and hence the molecular weight of a volatile salt, usually a chloride, of the element.

Let x and E be the valency and equivalent of the element, M. Then, Ex = atomic weight of the element.

Let MCl_x be the formula of the chloride.

$\therefore$ molecular weight of the chloride $= Ex + 35.46x$.

$$x = \frac{\text{Mol. wt. of chloride}}{E + 35.46} = \frac{2 \times \text{vapour density}}{E + 35.46}$$

Example.—*The vapour density of boron chloride is* 59. *The equivalent of boron is* 3.607. *Find the atomic weight of boron.*

Let the valency of the element be x and the fomula of the chloride BCl_x. The atomic weight of B is 3.607x. The molecular weight of the chloride is (3.607x+35.46x) and is equal to 2 × 59.

$\therefore$ $3.607x + 35.46x = 2 \times 59$, whence $x = 3.02 = 3$ (to nearest integer),

$\therefore$ the atomic weight $= 3.607 \times 3 = 10.82$.

(iv) **By Mitscherlich's law of isomorphism** (1820).—Substances are said to be isomorphous when they have the same crystalline structure. Thus, zinc sulphate $ZnSO_4,7H_2O$, and ferrous sulphate $FeSO_4,7H_2O$ are isomorphous, so also potash alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$, and chrome alum $K_2SO_4,Cr_2(SO_4)_3,24H_2O$, potassium sulphate, K_2SO_4, and potassium chromate, K_2CrO_4 ; also the phosphate and arsenate of sodium, Na_3PO_4, $12H_2O$ and Na_3AsO_4, $12H_2O$.

Criteria of isomorphism.—(i) *Similarity of crystalline structure.*

(ii) *Formation of mixed crystals*—From a solution of isomorphous compounds (*potash alum and chrome alum,* for example) homogeneous crystals separate containing varying amounts of either substances.

(iii) *Formation of overgrowths*—A crystal of a substance is found to grow in size when suspended in a solution of an isomorphous compound—a crystal of chrome alum, for example, is covered with layers of potash alum when suspended in a solution of the latter.

Law of Isomorphism.—*An equal number of atoms combined in the same way produce the same crystalline form which is independent of the chemical nature of the atoms but dependent upon their number and position.*

Isomorphous substances are usually represented by similar formulæ, e.g., Ag_2S and Cu_2S.

The law may be applied in two ways :—

(i) When an element displaces another in a compound *without changing its crystalline form,* the law asserts that one element replaces another *atom for atom,* that is, the number of atoms in the replacing amounts w and w′ respectively of the elements A (at. wt. a) and B (at. wt. b) are the same. $\therefore$ $w/a = w'/b$, or $w/w' = a/b$.

$$\therefore \frac{\text{replacing wt. of an element A}}{\text{replacing wt. of an element B}} = \frac{\text{at. wt. of A}}{\text{at. wt. of B}}$$

Suppose the percentages of two elements A (at. wt. a) and B (at. wt. b) in the two isomorphous compounds AX and BX are m and n respectively.

In AX, $A = m$; $X = (100-m)$. When $X = 1$, $A = m/(100-m)$

In BX, $B = n$; $X = (100-n)$. When $X = 1$, $B = n/(100-n)$

i.e., $m/(100-m)$ and $n/(100-n)$ are the replacing amounts of A and B respectively.

$\therefore$ $m/(100-m) : n/(100-n) = a : b$.

Hence atomic weight may be determined by analysis of isomorphous compounds.

Example.—Potassium selenate (containing 35.75% selenium) is isomorphous with potassium sulphate (containing 18.39% sulphur). Assuming the at. wt. of sulphur to be 32 find the at. wt. of selenium.

In potassium sulphate S = 18.39 ; the rest, i.e., K and O = 81.61.

In potassium selenate Se = 35.75 ; the rest, i.e., K and O = 64.25.

$\therefore$ when K and O = 1, S = 0.2253; Se = 0.5565 i.e., 0.2253 and 0.5565 are the replacing quantities of S and Se respectively.

$$\therefore \frac{\text{atomic wt. of Se}}{\text{atomic wt. of S}} = \frac{0.5565}{0.2253} \text{ or } \frac{\text{at. wt. of Se}}{32} = \frac{0.5565}{0.2253}$$

$\therefore$ at. wt. of Se = 79 nearly.

Alternatively, Potassium sulphate is K_2SO_4; and hence K_2SeO_4 is the formula for the selenate.

Molecular weight of $K_2SeO_4 = 2 \times 39 + x + 4 \times 16 = 142 + x$, where x is the atomic wt. of selenium.

$$\therefore \text{ the \% of Se} = 35.75 = \frac{100x}{142+x} \qquad \therefore \; x = 79 \text{ nearly.}$$

(ii) The *valency* of two elements forming isomorphous compounds is the same. Hence knowing the valency of one element, that of the other is found out; atomic weight is then found out from the relation:

atomic weight = equivalent weight × valency.

Thus, ferric oxide is isomorphous with aluminium oxide Al_2O_3 in which aluminium is trivalent; formula for ferric oxide should be Fe_2O_3 with trivalent iron.

(v) By reference to the position of an element in the periodic table:

As stated above, the atomic weight of an element = equivalent weight × valency—valency is a small whole number. In the light of his wide chemical knowledge Berzelius (1830) could correctly fix the right multiple (by which the equivalent weight is to be multiplied) in the case of few elements only, but in absence of any guiding principle there was a great deal of confusion as to the correct multiple. The discoveries of Dulong and Petit's law (1819) and Mitscherlich's law of isomorphism (1820) at about the same period, above all the application of Avogadro's hypothesis by *Cannizzaro* (1858), offered methods of finding the approximate atomic weights by means of which the correct multiple of the equivalent could be determined. The publication of **Prout's hypothesis** in 1815 that **the atomic weights of the elements are whole multiple of that of hydrogen** gave a stimulus to the determination of atomic weights. The hypothesis was rejected by the classical experimental researches of *Stas* (1860) on the equivalent and atomic weights. The publication of periodic table of Mendeleef in 1869 gave yet another impetus to experimental activities. Lastly, mention should be made of the precision work of *T. W. Richards* of Harvard University in the determination of atomic weights.

Molecular weight—Molecular weight of a substance is the sum of the atomic weights of all the atoms contained in a molecule, and consequently the molecular weight of a substance is also a relative weight based on the same standard of comparison as is used for the atomic weight. *The molecular weight of a substance may,* therefore, *be defined as the weight of a molecule of the substance relative to the weight of the oxygen atoms as* 16.0000.

Sulphuric acid, H_2SO_4, for example, contains 3 atoms of hydrogen, 1 atom of sulphur and 4 atoms of oxygen; hence its molecular weight

$$= 2 \times 1.008 + 32.066 + 4 \times 16 = 98.082.$$

The molecular weight of a substance in grams is referred to as the **am molecular weight** or the **gram molecule** or simply as a **mole.**

The gram-molecular weight of any gas or vapour occupies 22.4 litres at N.T.P. This is called **gram-molecular volume** or simply **molar volume.**

The atomic and molecular weights, as stated above, refer to relative weights only, but they are related to the absolute weights of the atom and molecules. 1 gram atom or 1 gram molecule of a substance always contains a constant number of individual atoms or molecules—this constant, called **Avogadro number,** *is defined as the number of individual molecules in* 1 *gram molecule of a substance ;* its value is 6.023×10^{23}. The number of individual atoms in 1 gram atom is also equal to this number. The absolute weight of an atom or a molecule is obtained by dividing the atomic or molecular weight of a substance by the Avogadro number. Absolute weight of :

a hydrogen molecule $= 2.016/6.023 \times 10^{23} = 0.3347 \times 10^{-23}$ gm.

a hydrogen atom $= 1.008/6.023 \times 10^{23} = 0.1673 \times 10^{-23}$ gm.

The absolute weight of an atom = the atomic weight of the element multipled by 0.1673×10^{-23} gm.

Thus the absolute weight of a carbon atom $= 12 \times 0.1673 \times 10^{-23}$ gm.

1 c.c. of hydrogen at N.T.P., weighing 0.00009 gm. contains about 5×10^{19} hydrogen atoms.

Exercises

1. 0.218 gm. of magnesium when dissolved in HCl, gave 218.2 c.c. of hydrogen collected over water, at 17°C and 754.5 mm. pressure. Find the equivalent of magnesium. Aqueous tension at 17°C = 14.4 mm.

Volume of hydrogen = 218.2 c.c. ;
Its pressure = 754.5 − 14.4 = 740.1 mm. ;
Its temperature = 17°C = 273 + 17 = 290° abs.
Let the volume at N.T.P. = v c.c.

$$\therefore \quad \frac{v \times 760}{273} = \frac{218.2 \times 740.1}{290}, \text{ whence } v = 200 \text{ c.c.}$$

Weight of 200 c.c hydrogen at N.T.P. = 200 × 0.00009 gm.

$$\therefore \quad \text{equivalent of magnesium} = \frac{0.218}{200 \times 0.00009} = 12.12.$$

2. The chloride of an element was converted quantitatively into the corresponding oxide and the following figures were obtained : 0.1827 gm. of the chloride gave 0.1057 gm. of the oxide. Calculate the equivalent of the element.

Cambridge University.

Let x be the equivalent ; then, $(x+35.5)$ gms. of the chloride give $(x+8)$ gms. of the oxide, where 35.5 and 8 are the equivalents of chlorine and oxygen respectively.

$$\therefore \quad \frac{x+8}{x+35.5} = \frac{0.1057}{0.1827}, \text{ when } x = 29.74$$

3. The vapour density of the chloride of an element M is 66 and the oxide of the element contains 53% of the element. Calculate the valency and the probable atomic weight.

London University.

47 gms. of oxygen unite with 53 gm. of the element.
∴ 8 gms. of oxygen unite with 53 × 8/47 or 9 gms. of the element.
∴ the equivalent of the element is 9.
Let the valency of the element be x.
∴ its atomic weight = valency × equivalent = $9x$.

Suppose the formula of the chloride is MCl_x.
∴ $9x + 35.5x = 132$, whence $x = 3$.

4. 0.1 g. of a mutal of which the specific heat is 0.214, on solution in hydrochloric acid displaced 124.4 c.c. of dry hydrogen at N.T.P. Calculate the atomic weight of the metal.

Calcutta, '53

Equivalent weight of the metal = 0.1/124.4 × 0.00009 = 8.933
Rough atomic weight = 6.3/0.214 = 29.44
∴ valency = rough atomic weight/equivalent weight = 29.44/8.933
= 3.296 = 3, since valency is an integer.
∴ exact atomic weight = 8.933 × 3 = 26.80.

5. A volume of 33.6 c.c. of phosphorus vapour weighs 0.0625 gm. at 546°C and 76 cm. pressure. What is the molecular weight of phosphorus and what is its atomicity ?

Let the volume of phosphorus vapour at N.T.P. = v c.c.

$$\text{Then, } \frac{v\times 760}{273} = \frac{33.6\times 760,}{(273+546)} \quad \therefore \; v = 11.2 \text{ c.c.}$$

Gram-molecular weight of any gas or vapour occupies 22.4 litres at N.T.P.

$$\therefore \text{ molecular weight of phosphorus vapour} = \frac{22.4\times 0.0625}{0.0112} = 125 \text{ gm.}$$

$$\text{Atomicity} = \frac{\text{molecular weight}}{\text{atomic weight}} = \frac{125}{31} = 4.03 = 4 \text{ (to nearest integer).}$$

---

6. What is meant by the equivalent weight of an element and how is it related to its atomic weight ? Describe an experiment to determine the equivalent of copper. What further facts and reasonings are required to fix its atomic weight ?

7. What do you mean by the term atomic weight ? State clearly the reasonings employed in deriving the atomic weight of an element. What were the earlier difficulties ?

8. "*The atomic weight of an element is the number of times one atom of it is heavier than the sixteenth part of the atom of oxygen*". Explain how this definition has arisen.

9. 10.788 g. of metallic silver (at. wt. 107.88) when heated in chlorine, yielded 14.3337 g. of silver chloride. Calculate the atomic weight of chlorine. 35.457

10. 0.3697 g. of Al liberated 0.04106 g. of H_2 on being dissolved in a strong solution of sodium hydrate ; find the at. wt. of Al. 27.009

11. 0.117 g. of a metal when dissolved in dilute hydrochloric acid evolved 117 c.c. of dry hydrogen gas at 12°C and 766 mm. Find the equivalent of the metal 11.5

12. 1.113 g. of Cu combine with 0.28 g. of O_2. Calculate the equivalent of copper. *Lond. Mat.* 31.8.

13. Magnesium oxide contains 60% magnesium. What is its equivalent weight ? 12

14. 0.24 g. of a metal (at. wt. 24) displaces 224 c.c. of H_2 at N.T.P. from an acid. What is the valency of the metal ? 2

15. The hydride of an element (at. wt. 31) contains 8.82% H_2. What is the valency of the element ? 3

16. In an experiment 0.49 gm. of a metal when dissolved in HCl gave 295 c.c. of dry hydrogen at 22°C and 752 mm. of Hg. The sp. ht. of the metal was found to be 0.152. Calculate the equivalent and at. wt. of the element.
Eq. wt. = 20.15 ; *at. wt.* = 40.3

17. The chloride of a metal contains 54.42% chlorine (at. wt. 35.5). The vapour density of the chloride is 8.16 (O = 1). Calculate the equivalent of the metal and the molecular formula of the chloride.
Madras Inter. ; *eq. wt.* 29.73 ; MCl_4

18. 0.2213 gm. of a metallic chloride required 0.510 gm. of silver nitrate to precipitate exactly the chlorine. The sp. ht. of the metal was 0.057. Find the equivalent, atomic weight and valency of the metal.
(At. wt. of Ag. 108 and that of Cl_2 35.5) 38.24 ; 114.72 ; 3

19. 4.215 gm. of a metallic carbonate were heated in a hard glass tube and the carbon dioxide evolved was collected over mercury. It was found to measure 1336 c.c. at 700 m.m. and 27°C. What was the equivalent of the metal ?
Madras Inter. ; 12.15

20. When 0.6 gm. of magnesium was treated with dilute HCl and the hydrogen evolved was collected over water in an eudiometer at 755 mm. and 20°C the volume of the gas was found to be 626 c.c. The height of water in the eudiometer was 200

m.m. Find the equivalent weight of magnesium. Aqueous tension at 20°C is 17.5 mm. 12

21. An element X forms a chloride which is isomorphous with potassium chloride and contains 25.87% chlorine. Calculate atomic weight of X. 101.7

22. The oxides of two metals A and B are isomorphous. The metal A whose atomic weight is 52 forms a chloride whose vapour density is 79. The oxide of the metal B contains 47.1% of oxygen. Calculate the atomic weight of B.
Rangoon Inter. ; 27

23. When 3.565 gm. of a compound $MSO_4.xH_2O$ was heated to 100°C, it gave 2.522 gm. of $MSO_4.3H_2O$. The latter compound when further heated to 150°C gave 2.00 gm. of the compound $MSO_4.H_2O$. Find the equivalent of M and the value of x. *Eq. wt.* 12 ; x = 7

24. In an experiment 2.470 gm. of copper oxide was obtained by oxidising 1.986 gm. of copper by nitric acid ; 0.335 gm. of copper was precipitated by 0.346 gm. of zinc from a solution of copper suplhate. Find the equivalents of copper and zinc. Cu = 32.8 ; Zn = 33.88

25. An oxide of a metal contains 30% oxygen. Its chloride contains 65.5% chlorine. 100 c.c. of the vapour of the chloride at N.T.P. weigh 0.72 gm. The sp. ht. of the metal is 0.114. What are its equivalent, atomic weight, and the formula of the chloride. Eq. wt. = 18.67 ; at. wt. = 56 ; MCl_3

26. 10.1 c.c. of dry chlorine gas at 15°C and 750 mm., were absorbed by potasium iodide solution. The liberated iodine produced 0.1982 gm. of silver iodide. Silver iodide contains 54.04% iodine and the equivalent of chlorine is 35.5. Find the equivalent of iodine. Mol. wt. of Cl_2 is 71. 127.0

27. Two salts, each containing potassium, oxygen, and one another element, were found to be isomorphous. One contained 28.2% potassium and 25.6% chlorine ; the other contained 24.7% potassium and 34.8% manganese. What value for the atomic weight of maganese is indicated by these data ? 55

28. The equivalent weight of a volatile metal is 100.3. The specific heat of the metal is 0.033. 0.25 gm. of the metal occupies 79.5 c.c. at 500°C and 760 mm. Calculate the atomic weight of the metal and the molecular weight of its vapour.
At. wt. = 200.6 ; mol. wt. = 199.5

29. 0.25 g. of an element when heated in oxygen produced 0.917 g. of a gaseous oxide. One litre of this oxide at N.T.P. weighs 1.98 g. Calculate the equivalent and atomic weight of the element. Eq. wt. 3 ; at. wt. 12

30. 0.0396 gm. of a metal was completely dissolved in HCl, and the hydrogen evolved was mixed with oxygen and sparked. 13.75 c.c. of dry oxygen measured at 27°C and 681 mm. pressure were required for complete combustion.

Find the equivalent weight of the metal. *Mysore Inter.* ; 19.8

31. 2.67 gm. of the chloride of a metal is heated with concentrated sulphuric acid until a residue of the sulphate of the metal weighing 3.42 gm. is obtained. Calculate the equivalent weight of the metal. 9

32. A metal M which is divalent in its ordinary salts, forms an oxide which contains 90.66% of the metal. When 13.70 gm. of its oxide were treated with nitric acid, 13.24 gm. of the nitrate were formed, and an insoluble residue weighing 4.78 gm. was left. The residue was shown by analysis to be another oxide of M containing 86.61% of M. From these data calculate the formulæ of the two oxides and the atomic weight of M. M_3O_4 ; MO_2 ; at. wt. = 207

33. 1.560 gm. of a liquid chloride of phosphorus were decomposed by excess of water. The resulting liquid, after adding silver nitrate, filtering, washing and drying the precipitated silver chloride, gave 4.883 gm. of silver chloride. Calculate the equivalent of phosphorus, assuming the equivalents of silver and chlorine to be 108 and 35.5 respectively. 10.44

34. Define equivalent and atomic weights. State Dulong and Petit's law and discuss its importance. The chloride of a metal M, contains 20.2 per cent of the metal. Its specific heat is 0.224. What is the accurate atomic weight of the metal ? If the vapour density of the chloride is 66.7, what is its molecular formula ?
Punjab, '51 ; at. wt. 26.9 ; MCl[illegible]

35. A certain metal forms two oxides. When 0.5 g. of the first oxide was heated in hydrogen, 0.1687 g. of water was obtained, while 0.4 gm. of second oxide under similar conditions yielded 0.1000 g. water. Calculate the equivalent of the metal.
Gauhati 1952. 18.66 ; 28

36. 0.3 gm. of a mixture of sand and magnesium gave 180 c.c. of hydrogen at 10°C and 750 mm. Given that the equivalent of magnesium is 12, and that sand has no action on the acid. Find the percentage of sand in the mixture. 38.8%

37. How much lime could be obtained from 0.7 gm. of pure calcite? Equivalent weight of calcium is 20. 0.392 gm.

38. Ferrous sulphate combines with ammonium sulphate to form a double sulphate which is isomorphous with the compound $CuSO_4.(NH_4)_2SO_4.6H_2O$ and which contains exactly one-seventh of its weight of iron. Find the atomic weight of iron. 56

39. An element forms a hydride whose vapour density is 17, and which contains 16/17ths of the element. There is no other compound whose gm. molecule contains less of the element than this compound does. What is its most probable atomic weight? 32

40. 363 c.c. of H_2 at 15°C and 756 mm. were liberated from dilute H_2SO_4 by 1 g. of zinc ; 0.973 g. of Cu was deposited by the action of a solution of copper sulphate on 1 gm. of zinc. Calculate the equivalents of zinc and copper.
Lond. Mat. Zn 32.44 ; Cu 31.56

41. 1 g. of the chloride of a bivalent metal when treated with excess of silver nitrate, gave 0.965 g. of AgCl. Calculate atomic weight of metal, Ag = 107.9 and Cl = 35.5. *Punjab Inter.*, 1932 ; 226.2

42. 20 gm. of tin were treated with dilute hydrochloric acid. When 1.12 litre of hydrogen at N.T.P. has been evolved the reaction was stopped, and the weight of tin remaining was found to be 14 gm. The chloride of tin was found to have a vapour density of 94.5. Find the atomic weight of tin. 119

43. On heating in contact with tin, sulphuretted hydrogen (density 17) is converted into hydrogen without change of volume. Calculate the equivalent weight of sulphur. 16

44. Explain the terms 'atomic weight' and 'equivalent weight'. Discuss the various methods by which the atomic weight of an element may be determined. 2.445 gm. of an acid reacted with 2.11 gm. of calcium carbonate, of which the equivalent is 50. What is the equivalent of the acid? 57.94

45. 0.1166 gm. of the chloride of a metal was dissolved in water, and 21.0 c.c. of N/10 silver nitrate were needed for the complete precipitation of the chlorine as silver chloride. The specific heat of the metal was 0.15. Calculate the equivalent weight and the atomic weight of the metal. Eq. wt. 20.00 ; at. wt. 40.00

46. State the relationship between the atomic weight, equivalent weight, and valency of the element. 0.1755 g. of a bivalent metal and 0.1316 g. of a trivalent metal when separately placed in dilute hydrochloric acid, yielded the same volume of hydrogen, viz., 190 c.c. at 27°C and 720 mm. pressure. Find the equivalent and atomic weights of the metals. *Calcutta* '52

Bivalent metal : eq. wt. 12 ; at. wt. 24 ; trivalent metal : eq. wt. 9 ; at. wt. 27.

47. Define the term atomic weight. The oxide of an element contains 28.6% oxygen and the vapour density of its chloride is 55.5. Calculate atomic weight of the element. *Punjab* '48 ; 39.94

48. The chloride of an element contains 37.32 per cent chlorine. The vapour density of the chloride is 190(H = 1). Specific heat of the element is 0.0276. Find the atomic weight of the element and the formula of the chloride.
Ajmer Inter. 1931 ; 238.56 ; MCl_4

49. Define (a) atomic weight, and (b) equivalent weight of an element. How are they related to each other? *Bombay* 1953

50. By converting pure silver into silver nitrate Richards found the ratio Ag : $AgNO_3$ = 1 : 1.57479. Calculate the atomic weight of silver, assuming that for nitrogen to be 14.008. 107.88

IX

MOLECULAR WEIGHTS

The *normal density* of a gas is the weight of 1 litre of the gas at N.T.P. The normal density of hydrogen is 0.0899 g. or 0.09 g. approximately.

The *relative density*, also called vapour density, of a gas

$$= \frac{\text{normal density of the gas}}{\text{normal density of } H_2} = \frac{\text{normal density of the gas}}{0.09}$$

$\therefore$ normal density of a gas = the relative density $\times 0.09$

i.e. weight of 1 litre of a gas at N.T.P. = the relative density $\times 0.09$.

Suppose M = molecular weight of a gas in gms.

D = normal density of the gas.

V_m = molar volume. $\therefore$ $V_m = M/D$.

For H_2, $M = 2.016$ and $D = 0.09$ $\therefore$ $V_m = 2.016/0.09 = 22.4$ litres.

For O_2, $M = 32$ and $D = 1.429$ $\therefore$ $V_m = 32/1.429 = 22.4$ litres.

By Avogadro's hypothesis V_m is the same for all gases, hence

$M = 22.4D$, $\therefore$ $M = 22.4 \times 0.09 \times$ relative density

or $M = 2.016 \times$ relative density.

Molecular weights from density measurements.—The calculation is usually based on the relations :

(i) $M = 2.016 \times$ relative density,

(ii) $M = 22.4 \times D$, where D = normal density,

(iii) $M = wRT/PV$, from gas equation $PV = nRT = wRT/M$,

where P = pressure in atmosphere ; V = volume in litres ; w = weight of substance ; $R = 0.082$ litre-atmosphere ; T = temperature in absolute degrees.

Determination of Gas Densities :—Regnault's method.—The method is used to determine density of *permanent gases*. The apparatus consists of 2 glass globes, as nearly equal in weight and capacity (about 2 litres) as possible, suspended from the arms of a balance. The globe A is fitted with a stop-cock and is used to contain the gas whose density is determined ; it volume is obtained by weighing it filled with water. B is a compensating globe used as counterpoise to check the effect of any change in atmospheric conditions ; B is filled with air at normal pressure and sealed (fig. 40).

The globe A is first evacuated and the accurately counterpoised by adding weights to the scale-pan above B. The globe A is then filled with the pure and dry gas (at a given temperature and pressure) and additional weights are put on the pan above B to restore the balance back to equilibrium—these additional weights

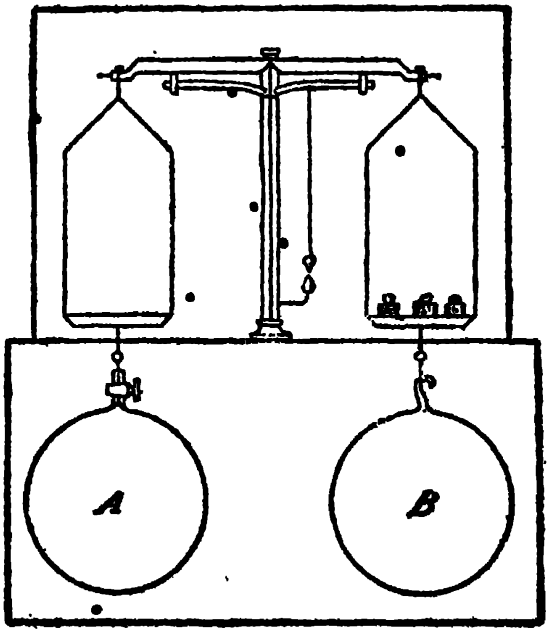


Fig. 40

is the weight of the known volume of gas in globe A. The density of the gas is obtained by dividing the weight by volume. [The *normal density* of a gas is determined by weighing a known volume of the gas measured *at N.T.P.* The *relative density* of a gas may either be calculated by dividing the normal density by that of hydrogen, or it may be found out by first weighing the globe A, full of the gas, and then full of hydrogen under the same conditions, and dividing the weight of the gas by that of hydrogen—in the latter method it is not necessary to know the volume of the globe A.]

Vapour densities and molecular weights.—(1) **Victor Meyer's method.**—Relative density of a **volatile liquid** is generally determined by this method.

In this method the vapour of a known weight of a *volatile* substance is allowed to displace an equal volume of *air* which is collected at the room temperature and pressure. The apparatus (fig. 41) is a long glass tube ending in a bulb at the bottom and having a side tube. In making a determination, the apparatus is cleaned and dried and a little sand placed in it. The open end of the tube is then closed by means of a cork, and the apparatus is placed in a wider copper jacket in which a liquid boils—its boiling point being about 20°C higher than that of the substance taken for the experiment. The side of the glass tube now dips under water in a trough. When a steady state is reached i.e., when no further bubble escapes through the side tube, a graduated tube filled with water is inverted over the side tube, and a small stoppered bottle containing a known weight of the substance (about 0.1 gm.) is *quickly* introduced into the apparatus, and the cork replaced. The stopper opens automatically and the liquid vaporises quickly—the vapour displacing an equal volume of air which is collected in the graduated tube—the temperature and the barometric pressure being noted.

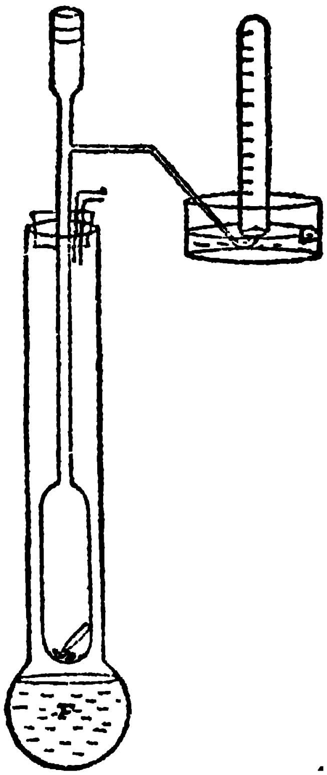


Fig. 41

Calculation.—Weight of the substance $= w$ gm.
Volume of air displaced $= v$ c.c.
Barometric pressure $=$ P mm.
Temperature of water $= t$°C.
Aqueous tension at t°C $= f$ mm.

$$\therefore \text{ Volume at N.T.P.} = \frac{v(P-f)\times 273}{(273+t)\times 760} \text{ c.c.} = v' \text{ (say)}$$

Weight of an equal volume of hydrogen $= v' \times 0.00009$ gm.

$\therefore$ vapour density $= w/v' \times 0.00009$.

Exercise.—0.22 g. of a substance when vaporised in Victor Meyer's apparatus displaced 45 c.c. of air collected over water at 20°C and 755 mm. pressure.

Calculate the mol. wt. of the substance. Aqueous tension at 20°C is 17.4 mm.
Punjab '45

(i) Volume of vapour = volume of air displaced

$$= 45 \times \frac{(755-17.4)}{760} \times \frac{273}{(273+20)} = 40.81 \text{ c.c. at N.T.P.}$$

Weight of same volume of H_2 at N.T.P. $= 40.81 \times 0.00009$ gm.

vapour density of the substance $= \frac{0.22}{40.81 \times 0.00009} = 60.$

molecular weight $= 2 \times 60 = 120.$

(ii) Volume of vapour = 40.81 c.c. at N.T.P.

40.81 c.c. at N.T.P. weigh 0.22 gm.

$\therefore$ 22.4 litres at N.T.P. weigh $\frac{0.22 \times 22.4}{0.04081}$ or 120.7 gm. which is the mol wt., since 1 gram molecular weight of any gas occupies 22.4 litres at N.T.P.

(iii) $PV = wRT/M$

P = pressure in atmospheres $= \frac{755-17.4}{260} = \frac{737.6}{760}$ atmosphere.

V = volume of vapour in litres = 0.045 litre

w = weight of substance = 0.22 g.

R = 0.082 litre-atmosphere ; $T = 273 + 20 = 293°$ absolute.

$$M \quad \frac{wRT}{PV} = \frac{0.22 \times 0.082 \times 293 \times 760}{0.045 \times 737.6} \quad 120.7.$$

(ii) **Dumas' method.**—The method is applicable to *easily volatalisable liquids* only. In this method a thin glass bulb (capacity about 200 c.c.) with a drawn out neck, is cleaned, dried, and weighed (fig. 42). By dipping the neck in the liquid whose density is required, and by alternate heating and cooling, about 100 c.c. of liquid is introduced into the bulb. The bulb is then held immersed in a constant temperature bath of water, oil or molten wax (temperature being 30°—40° above the boiling point of the liquid), so that the tip of the neck is above the surface of the bath. The liquid begins boiling, giving off vapour which completely displaces the air in the bulb.

When the evolution of vapour stops and the bulb is *full of vapour only*, the neck is sealed off—the temperature of the bath, and the barometric pressure at the time of sealing are noted.

The bulb is next removed from the bath, cleaned and weighed. Finally the neck is broken under the surface of previously boiled water—the water enters the bulb and fills it completely. The bulb full of water is weighed.

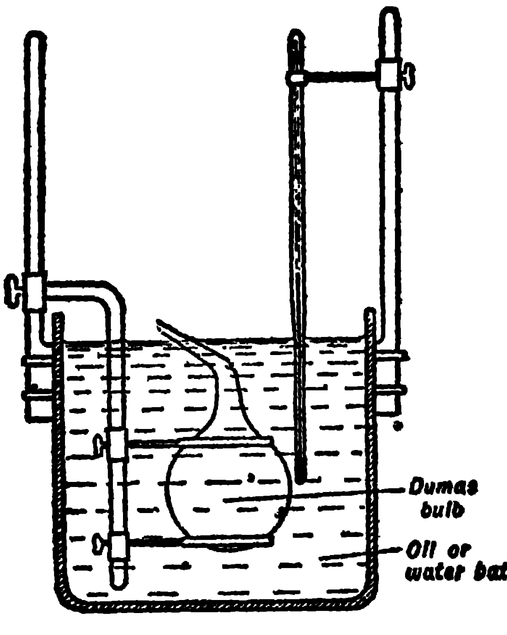


Fig. 42

Calculation.—Let the weight of bulb filled with air = a gm.
weight of bulb filled with vapour = b gm.
weight of bulb filled with water = c gm.
temperature of weighing = t°C
temperature of bath = t'°C
barometric pressure = P mm.

$\therefore$ volume of bulb at t°C = (c−a) c.c.

Volume of air filling bulb at N.T.P. $= (c-a) \times \frac{P}{760} \times \frac{273}{(273+t)} = A$ c.c.

Density of air at N.T.P. = 0.001293 gm./c.c.

$\therefore$ weight of A c.c. of air at N.T.P. $= 0.001293 \times A$ gm.

Weight of vacuous bulb $= (a - 0.001293 \times A)$ gm.

Weight of vapour filling the bulb at t°C and P mm pressure

$= [b-(a-0.001293 \times A)]$ gm.

Volume of this vapour at N.T.P. $= (c-a) \times \frac{r}{760} \times \frac{273}{273+t'} = V$ c.c.

normal density of vapour $= \frac{b-(a-0.001293A)}{0.001V}$ gm/litre

$\therefore$ mol. wt. $= 22.4 \times$ normal density.

Molecular weights in solution.—More common methods involved measurements of :

(i) *osmotic pressure of a solution ;*

(ii) *lowering of the vapour pressure of a solution ;*

(iii) *depression of the freezing point of a solution ;*

(iv) *elevation of the boiling point of a solution.*

(i) **Osmosis and osmotic pressure.**—A solution has a tendency to dilute itself ; when a solution is separated from a solvent by a semi-permeable membrane, there occurs a spontaneous flow of the solvent through the membrane from the solvent to the solution side—this spontaneous flow of solvent is known as *osmosis*, and was first observed by Abbe Nollet in 1748.

A *semipermeable membrane* is a medium which when used as a partition between a pure solvent and a solution freely lets through the solvent but not the solute. In the case of two solutions of different concentrations the flow of solvent is from low to high concentration of solute.

Abbe Nollet's experiment.—Osmosis was demonstrated by this experiment in which a semipermeable animal membrane (pig's bladdar) was stretched across the mouth of a thistle funnel ; the funnel was filled with a strong solution of cane sugar and inverted over a trough of distilled water (Fig. 43). Osmosis occurs and the flow of water through the membrane causes the level of solution in the stem A of the funnel to rise gradually until a steady definite maximum level is attained. When the steady state is reached, the hydrostatic pressure of the column of solution becomes equal to the pressure forcing the water in and is just sufficient to prevent the flow of more solvent into the solution. This pressure, developed as a result of osmosis, is known as the *osmotic pressure* of the solution.

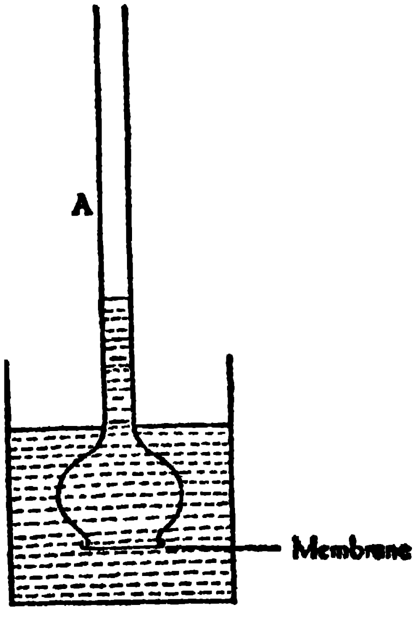


Fig. 43

In the light of the above experiment the *osmotic pressure of a solution may be defined as the excess pressure which must be exerted on the solution when* *a solution and a solvent are separated by a semi-permeable membrane in order to just prevent the flow of the pure solvent through the membrane into the solution.*

Measurement of osmotic pressure : Pfeffer's method.—Animal membranes are too weak to withstand fairly high pressure in actual measurements and easily give way. Copper ferrocyanide is an ideal semi-permeable membrane for this purpose.

Copper ferrocyanide is deposited on the walls of a porous (unglazed porcelain) pot, P ; the pot is then cemented to a glass tube, g, which in its turn is fitted with a calibrated air manometer, m. The pot is filled with the solution and then placed in a tank of distilled water at a constant temperature (fig. 44). Water flows into the solution and develops a high pressure. Sufficient time is given for the system to attain equilibrium and the osmotic pressure at the temperature of the experiment is read off from the manometer.

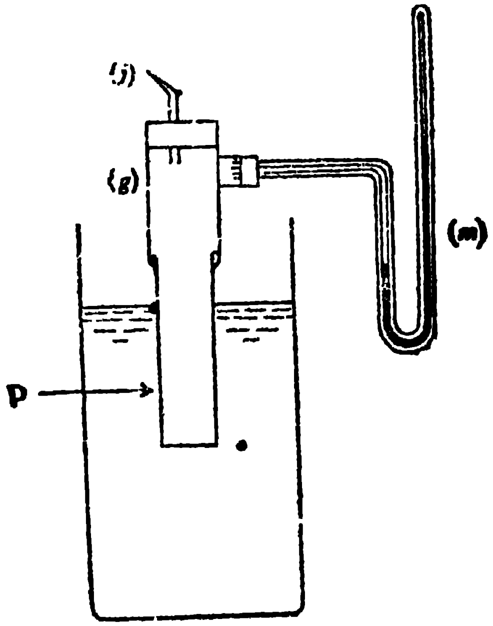


Fig. 44

Laws of osmotic pressure.—(i) *At a constant temperature the osmotic pressure of a solution is proportional to concentration.*

Let P = osmotic pressure ; C = concentration of a solution, expressed in moles per unit volume of the solution, and V = volume of the solution containing 1 mole of the solution, then C = $1/V$.

$\therefore$ P $\propto$ C, or P = constant $\times$ C, or PV = constant, at constant temperature. This is the analogue of Boyle's law.

(ii) *For a given concentration the osmotic pressure of a solution is proportional to the absolute temperature,*

P $\propto$ T or P = constant $\times$ T.

This is the analogue of Charles's law.

The two laws may be combined in the single equation :

PV = R′T, where R′ is a constant.

This equation which is similar to the gas equation PV = RT, is often called *van't Hoff* equation for dilute solutions ; the two constants R′ for solutions and R for gases, have the same value 0.082 litre-atmosphere. Hence the gas equation PV = RT is valid for dilute solutions, where P is the osmotic pressure.

This clearly shows the parallelism between the properties of solutions and gases, and therefore "the osmotic pressure of a dilute solution is equal to the pressure which

the dissolved solute would exert if it were a gas at the same temperature, and occupied the same volume as the solution".

For n gram molecules of the solute, $PV = nRT$.

It follows that equal volumes of solutions having the same osmotic pressure and at the same temperature contain equal number of molecules of solute. This is the analogue of Avogadro's hypothesis. These laws of osmotic pressure are valid for *dilute* solutions of *non-electrolytes* only and marked deviations are observed when :

(i) the solution is more concentrated than deci-normal ;

(ii) the solute associates or dissociates in solution.

Two solutions having the same osmotic pressure are known as **isotonic solutions.**

Molecular weight from osmotic pressure.—In the equation $PV = nRT$, $n = w/M$, where w = weight of solute in V litres of solution and M = molecular weight of the solute.

$$\therefore \quad PV = wRT/M \text{ or } M = wRT/PV.$$

P is expressed in atmospheres and R is equal to 0.082 litre-atmosphere.

Exercise.—The osmotic pressure of a 2 per cent solution of acetone in water is 590 cm. of mercury at 10°C. What is the molecular weight of acetone ?

Cal. B.Sc., '35

$$P = \frac{590}{76} \text{ atmosphere} \; ; \; V = \frac{100}{1000} = 0.1 \text{ litre} \; ;$$

$$R = 0.082 \text{ litre-atmosphere} \; ; \; T = 273 + 10 = 283° \text{ abs.} \; ; \; m = 2 \text{ gm.}$$

$$M = \frac{wRT}{PV} = \frac{2 \times 0.082 \times 283 \times 76}{0.1 \times 590} = 59.77.$$

(ii) **Lowering of vapour pressure.**—When a non-volatile solute is dissolved in liquid the vapour pressure of the latter is lowered—the lowering of the vapour pressure being proportional to the concentration of the added solute.

If p° is the vapour pressure of a pure solvent and p, that of the solution, at a given temperature, then $(p^\circ - p)$ is the lowering of vapour pressure, and $(p^\circ - p)/p^\circ$ is known as the *relative lowering of vapour pressure.*

Raoult's law.—*Raoult's law* states that the *relative lowering of the vapour pressure of a solution is equal to the mol fraction of the solute in solution.*

If N and n be the number of moles of solvent and solute respectively, then mol fraction of solute $= n/(N+n)$.

Hence, by Raoult's law, $\dfrac{p^\circ - p}{p^\circ} = \dfrac{n}{N+n}$

or $\dfrac{p^\circ - p}{p^\circ} = \dfrac{n}{N}$ approximately for dilute solutions.

If the solution consists of w gms. of solute (mol. wt. m) and W gms. of solvent (mol. wt. M), then

$$\frac{p^\circ - p}{p^\circ} = \frac{w/m}{W/M}$$

The molecular weight of a solute may be determined from the above expression by making a solution of known weights of solute and solvent (mol. wt. of solvent being known) and by measuring the vapour pressure of the solution and the solvent.

(ii) **Depression of the freezing point.**—The freezing point of a solution is less than that of the pure solvent. *The lowering of freezing point of a solution is proportional to the concentration of the solute.*

$$dt \propto C \quad \therefore \quad dt = KC,$$

where dt = depression of freezing point ;

C = molal concentration, i.e., the number of gram molecules of solute dissolved in 1000 gms. of solvent. K = is a constant, called *molal depression of freezing point* or *cryoscopic constant,* i.e., the depression of freezing point caused by dissolving 1 gram molecule of a solute in 1000 gms. of the solvent.

Let W gm. of solvent contain in dissoved state w gms.

(molecular weight m) or w/m gram molecules of solute.

$\therefore$ 1000 gm. of solvent contain (w/m) × (1000/W) gram molecules of the solute.

$$\therefore \quad C = \frac{w \times 1000}{m \times W} \text{ or } dt = K.\frac{w \times 1000}{m \times W}.$$

$$\therefore \quad m = K.\frac{1000w}{dt\ W} \ldots\ldots\ldots \text{(i), also } K = \frac{0.002T^2}{l} \ldots\ldots \text{(ii)}$$

where T = freezing point of solvent in degrees absolute, and l = latent heat of fusion of solvent per gram. From equation (i) and (ii) m can be calculated.

The equation holds good for *dilute* solutions of *non-electrolytes* only—*the solution on freezing must deposit crystals of pure solvent only.*

Molal cryoscopic constants for few solvents are as follows :

Water	1.86	Benzene	5.12
Acetic acid	3.90	Camphor	40.0

Exercise.—1.25 gm. of a hydrocarbon dissolved in 29.7 c.c. of benzene depressed the freezing point from 5.4°C to 3.52C. Calculate the mol. wt. of the hydrocarbon. Latent heat of fusion of benzene is 29.1 cals. per gram and the density 0.878 gm. per c.c.

$$K = \frac{0.002T^2}{l} = \frac{0.002(273+5.4)^2}{29.1} = 5.325$$

$$w = 1.25 \text{ ; } W = 29.7 \times 0.878 \text{ gm ; } dt = 5.4 - 3.52 = 1.88°C$$

$$m = K\frac{w \times 1000}{W \times dt} = \frac{5.325 \times 1.25 \times 1000}{29.7 \times 0.878 \times 1.88} = 135.7$$

Determination of Lowering of Freezing Point.—A very sensitive **Beckmann thermometer** is used in the determination. It has a large bulb and only six degrees on the scale—each degree is graduated into 100 division. There is a reservoir at the top of the capillary tube from which mercury can be drawn into the tube and bulb when lower temperatures are required or into which mercury can be made to overflow if higher temperatures are used. The actual readings on the scale are immaterial, as their *difference* only is required.

Beckmann's Method.—An accurately weighed quantity of pure solvent (about 20 g.) is taken in a tube (fig. 45) which is fitted with a platinum stirrer and a Beckmann thermometer through a cork, so that the bulb is covered with liquid. The thermometer is previously *set* so as to get the freezing point of the pure solvent towards the top of the scale. The tube is fitted through a cork into a wide tube which simply acts as an air jacket and prevents too rapid fall in temperature. The tube is then placed in a freezing mixture (ice and salt) in a jar. The solvent is gently stirred—the stirrer in the freezing mixture is also worked and the thermometer observed. The mercury falls gradually to a certain point, when the solvent supercools slightly below its true freezing point. Vigorous stirring is then started when freezing commences and the mercury column at once runs up to the freezing point and remains stationary on the thermometer. It is then read off with a lens.

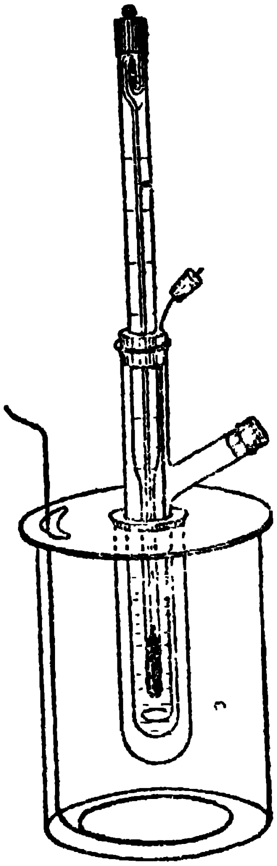


Fig. 45

The tube is then taken out and allowed to warm till the solid solvent melts. A weighed quantity of solute (about 0.2 g.) is then introduced through the side tube and dissolved in the solvent by stirring. The tube is then replaced in the air jacket which in its turn is placed in the freezing mixture. The solution is stirred and cooled as with the solvent and the freezing point of the solution read off. The difference between the two readings gives the depression of the freezing point.

(iv) **Elevation of boiling point.**—Since the boiling point of a liquid is the temperature at which its vapour pressure is equal to atmospheric pressure, a solution of which the vapour pressure has been lowered by the addition of a *non-volatile* solute, boils at a higher temperature than the solvent.

Elevation of boiling point of a solution is proportional to the concentration of the dissolved solute, i.e.,

$$dt \propto C \qquad \text{or} \qquad dt = K.C,$$

where dt = elevation of boiling point,

C = molal concentration, i.e., number of gram molecules of solute in 1000 gms of solvent ;

K = a constant, called molal elevation of boiling point or boiling point constant, caused by dissolving 1 gram-molecule of solute in 1000 gms. of solvent.

Let W g. of solvent contain w gm. (molecular weight m) or w/m gram molecules of the solute.

∴ 1000 g. of solvent contain $(w/m) \times (1000/W)$ gram molecules of solute.

$$C = \frac{w \times 1000}{m \times W} \text{ or } dt = K.\ \frac{w \times 1000}{m \times W}$$

$$\cdot\, m \quad K.\ \frac{1000\,w}{dt\ W} \ \ldots\ldots \text{(i) aiso } K = \frac{0.002T^2}{l} \qquad \text{(ii)}$$

T = boiling point of the solvent in degrees absolute, and

l = latent heat of vaporisation of the solvent per gram.

The equations hold good for *dilute* solutions of *non-volatile non-electrolytes* only.

Molal Boiling Point Constants for few solvants are as follows :

Ethyl alcohol	0.513	Acetone	1.72
Water	1.20	Benzene	2.63

Determination of elevation of boiling point.—Landsberger's method.—In this method the liquid is raised to its boiling point by passing a stream of vapour of the pure boiling solvent into it ; the vapour on condensation gives out latent heat of vaporisation which heats the liquid to its boiling point without any risk of superheating. The apparatus is shown in fig. 46. The pure solvent (about 5 c.c.) is taken in the graduated tube A, having an orifice just above the bulb ; the tube is fitted with a thermometer graduated in tenths of a degree and a delivery tube from the flask D in which the pure solvent is kept boiling. The tube is fitted with an outer jacket B which is attached to a condenser at C. The vapour of the pure solvent from the flask D where it is kept boiling passes into the solvent in the tube A and condenses there, its latent heat of vaporisation raising the liquid to its boiling point, which is read from the thermometer when the temperature becomes steady—the excess vapour escape through the orifice into the outer jacket B and provide a hot jacket round A and is finally condensed by the condenser C. After recording the boiling point of the solvent, the vapour is cut off and greater part of liquid in A is poured back into D, only about 5 to 7 c.c. being left behind. A weighed amount (about 0.2 g.) of solute is then added and dissolved in the liquid in A and the boiling point is again determined as before. The temperature is read off and immediately afterwards the supply of vapour is cut by disconnecting the flask D ; the burner from under the flask D, the thermometer and delivery tube from A, all are removed and the volume of the solution is read on the graduated tube and the weight of solvent calculated from the density. Usually successive determinations are made by passing in more vapour until the boiling point is again reached.

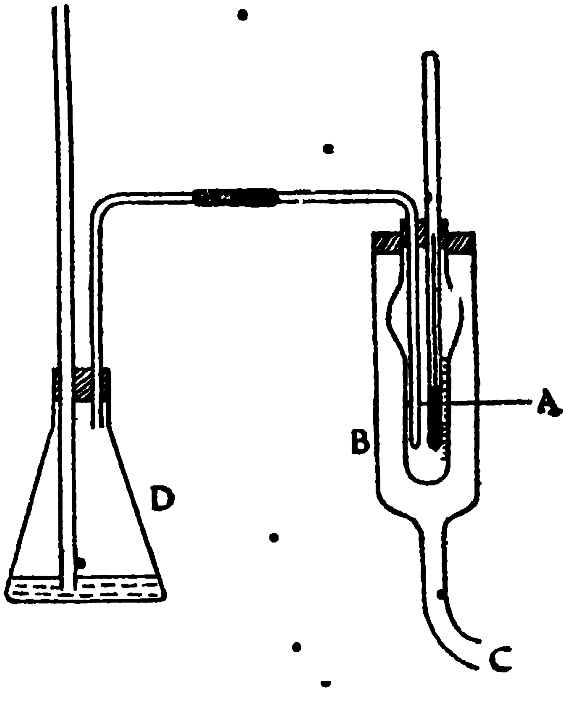


Fig. 46

Exercise.—A solution containing 0.5042 g. of a substance dissolved in 42.02 g. of benzene boils at 80.175°C. Calculate the mol. wt. of the substance. Benzene boils at 80°C and its latent heat of vaporisation is 94 cals. per gram.

$$K = \frac{0.002T^2}{l} = \frac{0.002(273+80)^2}{94} = 2.652$$

$$w = 0.5042 \text{ g} ; \ W = 42.02 \text{ g.} ; \ dt = 80.175-80 = 0.175°C$$

$$m = K\frac{w \times 1000}{W \times dt} = \frac{2.652 \times 0.5042 \times 1000}{42.02 \times 0.175} = 181.9.$$

Molecular weight by effusion method.—The method is based on the relation :

$$\frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

where t_2 and t_1 are rates of effusion of two gases of molecular weights M_2 and M_1 respectively.

Exercises

1. Explain what is meant by (a) molecular weight, (b) vapour density. What is the relation between the two ? Describe a method for the determination of the molecular weight of a volatile liquid.

2. 0.178 g. of a liquid is vaporised in Victor Meyer apparatus ; 28.6 c.c. of air was displaced and collected over water, at 15°C and 754 mm. Calculate (a) weight of 1 c.c. of vapour, (b) vapour density, (c) molecular weight of the substance. Aqueous tension at 15°C is 12.8 mm ; density of H_2 is 0.09 g./*l*.
(a) 0.006732 gm., (b) 74.8, (c) 149.6

3. 0.22 g. of a substance when vaporised displaced 45.0 c.c. of air measured over water at 20°C and 755 mm. Calculate molecular weight of the substance. Aqueous tension at 20° is 17.4 mm. *Punjab Inter*, 1945 ; 120.1

4. What is meant by gram molar volume ? 2.762 g. of a gas occupy 3.895 litres at 20°C and 780 mm. Calculate its molecular weight.
Punjab Inter, 1940 ; 17

5. Calculate the mean molecular weight of air, and its density at N.T.P. and at 27°C. Air contains 80% N_2 and 20% O_2 by volume.
Mean mol. wt. = 28.8 ; d = 1.286 g./*l* (N.T.P.) and 1.170 g./*l*. (27°C)

6. What is meant by osmotic pressure of a solution and how it is measured ? Calculate the osmotic pressure at 25°C of a solution containing 5 gms. of urea (mol. wt. 60) in a litre of solution. 2.036 atm.

7. A 4 per cent solution of ribitol in water is found to have the same osmotic pressure at 34°C, as a 5 per cent solution of glucose (mol. wt. 180) at 18°. Find the molecular weight of ribitol. *Cambridge Entrance School* : 152

8. Describe the effect of a non-volatile solute on (a) the freezing point, and (b) boiling point of a solvent. Describe how you would determine the molecular weight of (i) chloroform, (ii) glucose, and (iii) urea.

9. Explain how the molecular weight of a substance in solution may be determined from observations of the depression of freezing point. If 1 g. of a substance is dissolved in 15 gm. of water the freezing point is lowered by 0.37°C. What is the molecular weight of the dissolved substance ? The freezing point constant for water is 1.9. 342

10. A solution containing 0.7269 gm. of camphor (mol. wt. 152) in 32.08 gm. of acetone (boiling point 56.3°C) boiled at 56.55°C. What is molar elevation for acetone and its latent heat of vaporisation ? K = 1.677 ; *l* = 129.3 cal./g.

X

THE LAW OF MASS ACTION

Reversible reactions.—There are many chemical reactions of the type $A+BC = AB+C$ which do not go to *completion* in one direction but proceed only to a certain point since the opposing reaction $AB+C = A+BC$ can take place at the same time and under the *same* conditions as the direct reaction. A state of equilibrium is reached when the two opposing reactions balance each other :

$$A + BC \rightleftharpoons AB + C.$$

Thus, when a mixture of equivalent amounts of hydrogen and iodine is heated in a sealed bulb at 356°C, about 80 per cent of it is converted into hydrogen iodide, however long the heating is continued : $H_2 + I_2 = 2HI$. If hydrogen iodide is heated under the same conditions, only 20 per cent of it is decomposed : $2HI = H_2+I_2$. At this temperature hydrogen, iodine and hydrogen iodide are said to remain in *chemical equilibrium ; the equilibrium is independent of time.* The state of equilibrium obtains whether one starts with a mixture of hydrogen and iodine or with pure hydrogen iodide ; in other words, *the reaction is reversible,*—a reversible reaction can, therefore, proceed in either direction.

When the equilibrium is attained, the formation of hydrogen iodide, HI, from its elements and its decomposition into H_2 and I_2 take place *with equal and opposite speeds,* so that as much HI formed as is decomposed in a given time. Two opposing *reversible* reactions *balance* each other at equilibrium, which is written as : $H_2+I_2 \rightleftharpoons 2HI$, and the action is called a *balanced action.*

Steam is decomposed by red-hot iron giving hydrogen and ferroso-ferric oxide : $3Fe+4H_2O = Fe_3O_4+4H_2$, and *under the same conditions* the oxide of iron is reduced by hydrogen giving iron and steam : $Fe_3O_4+4H_2 = 3Fe+4H_2O$. A state of equilibrium is set up when as much steam is decomposed as is formed in a given time ;

$$3Fe+4H_2O \rightleftharpoons Fe_3O_4+4H_2.$$

Effect of insolubility or volatility.—Sometimes a reaction appears to go to completion instead of to a state of equilibrium. This is because of the *disturbance of the equilibrium state* when one or more of the products deposit as a precipitate owing to *insolubility* or pass into the gaseous state due to their *volatility,* and do no longer influence the reaction.

(i) When barium chloride solution is added to dilute sulphuric aicd the equilibrium : $BaCl_2 + H_2SO_4 \leftrightarrows BaSO_4 + 2HCl$, is disturbed owing to the precipitation of barium sulphate, and as a result the reaction seems to go to completion.

(ii) When strong sulphuric acid is added to common salt the equilibrium : $NaCl + H_2SO_4 \leftrightarrows NaHSO_4 + HCl$, is disturbed owing to escape of hydrogen chloride as gas and the reaction proceeds.

(iii) When limestone is heated in a closed vessel the following equilibrium : $CaCO_3 \leftrightarrows CaO + CO_2$, is reached owing to the reversibility of the reaction ; but when heated *in a current of air*, the carbon dioxide is carried away, and consequently calcium carbonate decomposes completely into CaO and CO_2.

(iv) As stated above, the following equilibrium : $3Fe + 4H_2O \leftrightharpoons Fe_3O_4 + 4H_2$, is set up, when steam is decomposed by red-hot iron in a closed vessel ; when however, a current of steam is passed over heated iron, the hydrogen is removed from the sphere of reaction with excess of steam and the iron may then be completely oxidised. If on the other hand, a current of hydrogen is passed over heated iron oxide, the reverse reaction proceeds to completion.

Irreversible reactions.—There are some reactions which proceed in one direction only ; they are classed as *irreversible reactions*. Potassium chlorate, for example, decomposes by heat into potassium chloride and oxygen, $2KClO_3 = 2KCl + 3O_2$. The reverse reaction, i.e., formation of $KClO_3$ from KCl and O_2 does not occur. Hydrogen peroxide decomposes irreversibly into water and oxygen :

$$2H_2O_2 = 2H_2O + O_2.$$

The law of mass action.—As stated above, the attainment of the state of equilibrium depends on the speed of a reaction. The principal factors which determine the speed of a chemical change are : *temperature, pressure, catalyst and concentration of reacting substances.*

The effect of mass was studied by Guldberg and Waage in 1367 who enunciated the *law of mass action* which states :

At a given temperature the rate of a chemical reaction is proportional to the active mass of the reactants.

The active mass is defined by the *molar concentration* of reacting substances, e.g., *in gram molecules per litre.*

Consider the reversible reaction ; $A + B \rightleftharpoons C + D$. According to the law of mass action, the speed of the forward reaction, v_1, with which A and B react depends on the concentrations of A and B, i.e.,

$$v_1 \propto [A]\,[B], \text{ or } v_1 = k_1\,[A]\,[B],$$

where k_1 is a proportionality constant for the forward reaction.

The concentration of a given substance A is denoted by its symbol in square brackets [A].

The products of the reaction B and C react to produce A and B. The rate of the backward reaction, v_2, depends on the concentration of B and C, i.e.,

$$v_2 \propto [C]\,[D], \text{ or } v_2 = k_2\,[C]\,[D].$$

where k_2 is a proportionality constant for the reverse reaction.

At equilibrium $v_1 = v_2$, $\therefore$ $k_1\,[A]\,[B] = k_2\,[C]\,[D]$

$$\therefore \quad K = \frac{k_1}{k_2} = \frac{[C]\,[D]}{[A]\,[B]}$$

The constant K is known as the *equilibrium constant or the law of mass action constant ; K is constant at a given temperature.*

In general, if n molecules of a substance takes part in a chemical reaction, the corresponding concentration term is raised to the nth power. Thus, in the reaction :

$$aA + bB \rightleftharpoons cC + dD, \quad K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

The magnitude of the equilibrium constant K is a measure to which substances react to form the products, i.e., *a measure of chemical affinity.*

The following example of a reversible reaction is highly illustrative :

$$Fe(NO_3)_3 + 3NH_4CNS \leftrightharpoons Fe(CNS)_3 + 3NH_4NO_3$$

Ferric nitrate and ammonium thiocyanate in solution produce ferric thiocyanate which is deep red in colour. The colour deepens greatly on the addition of an excess of either of the reactants, but if NH_4NO_3 is added, the reverse reaction takes place and the colour becomes distinctly paler.

Le Chatelier's principle.—The effect of change of temperature and pressure on chemical equilibrium can be predicted by *Le Chatelier's principle* which states :

If one of the conditions of a system in equilibrium be altered, the system will adjust itself in such a direction as partially to neutralise the change in condition.

(i) **Effect of temperature on equilibrium.**—Consider the synthesis of ammonia :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 22000 \text{ cals.}$$

This is an *exothermic* reversible reaction. When the temperature of the system in equilibrium is raised, then according to Le Chatelier's principle that change occurs which absorbs heat and tends to lower the temperature, i.e., the decomposition of ammonia into the elements is favoured, and when the temperature is lowered that change occurs which evolves heat, i.e., the formation of ammonia is favoured. In general, the principle predicts that *increase in temperature favours an endothermic change and decrease in temperature an exothermic change.*

(ii) **Effect of pressure on equilibrium.**—Consider the reaction.

$$\underset{\text{1 mole}}{N_2} + \underset{\text{3 moles}}{3H_2} \rightleftharpoons \underset{\text{2 moles}}{2NH_3}$$

A total of 4 molecules of nitrogen and hydrogen give 2 molecules of ammonia, that is, the formation of ammonia takes place with *decrease* in number of molecules and with a consequent *decrease in volume at a given temperature and pressure,* since pv = nRT ; if the system, on the otherhand, be kept at constant volume, the decrease in number of molecules would cause a decrease in pressure, since PV = nRT.

When pressure is applied to the system in equilibrium, then according to Le Chatelier's principle, that change occurs which causes a fall in pressure, i.e., a decrease in number of molecules and hence favouring increased formation of ammonia.

Hence, *increase of pressure on a system in equilibrium favours that change which takes place with decrease in volume.*

The decomposition of ammonia into nitrogen and hydrogen takes place with increase in number of molecules and with a consequent increase in volume, or if the volume is kept constant, it will cause an increase of pressure. When pressure is *lowered* on the system in equilibrium, that change occurs which takes place with an increase of pressure, i.e., with an increase in number of molecules and consequently decomposition of ammonia is favoured. Hence, *decrease of pressure favours the change which occurs with increase in volume.*

In all cases where the total volume is unchanged by a reaction, pressure has no influence on the equilibrium state. The equilibrium $H_2 + I_2 \rightleftharpoons 2HI$, for example, is independent of pressure.

(iii) **Effect on equilibrium of altering concentration.**—(a) *The effect of removing a substance from an equilibrium mixture.* Consider the reaction :

$$NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl.$$

The hydrogen chloride formed is a gas, and as it escapes, its concentration in the equilibrium mixture falls, and consequently, by Le Chatelier's principle, the equilibrium shifts in the direction which increases the concentration of hydrogen chloride ; this is a direction to the right, i.e., some more hydrogen chloride is formed. As the hydrogen chloride continues to escape, the forward reaction appears to go to completion.

(b) *The effect of adding a substance to an equilibrium mixture.* Consider the dissociation of phosphorus pentachloride.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

On adding chlorine, its concentration in the equilibrium mixture increases, and hence the equilibrium changes in the way as stated by Le Chatelier's principle, i.e., in the direction which reduces the concentration of chlorine ; the equilibrium, therefore, shifts to the left, forming some phosphorus pentachloride i.e., the extent of dissociation of PCl_5 is decreased. The addition of PCl_3 to the system has a similar effect.

The addition of one of the products of dissociation, therefore, reduces dissociation.

Abnormal vapour density.—A determination of the density of the vapour of a substance that undergoes thermal dissociation gives the density of the mixture of the products of dissociation, and not that of the original substance. One molecule of ammonium chloride, for example, dissociates on heating into one molecule of ammonia and hydrogen chloride :

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

The vapour would, therefore, occupy double the volume that would be expected if ammonium chloride volatilised unchanged ; the observed density for complete dissociation will be half the theoretical density and consequently the molecular weight would be half the expected value. Bineau found the vapour density 12.9 which gives a molecular weight of 25.8, about half the theoretical value. Pebal and Than confirmed the dissociation of NH_4Cl by separating NH_3 and HCl from the vapour by diffusion by the following arrangement :

Some solid ammonium chloride is heated in a tube d (fig. 47) divided into two parts by a porous plug of compressed solid ammonium chloride. Ammonia, being much lighter than hydrogen chloride, diffuses more rapidly than the latter, and hence the gas in the part Ad contains an excess of NH_3 and that in the part Bd an excess of HCl. A slow stream of nitrogen is passed through the tube c on both sides of the plug, so that a red litmus paper held at a′ becomes blue, and a blue litmus at b′ turns red. Baker found that absolutely dry ammonium chloride does not dissociate.

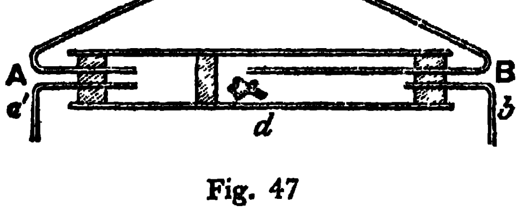


Fig. 47

Degree of dissociation.—When a gas dissociates, more molecules are produced : $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ and at constant temperature and pressure volume increases, since $PV = nRT$; consequently the density or the weight per litre decreases. The degree of dissociation, i.e., the *fraction of the total number of molecules dissociated*, is calculated as follows : Let us consider 1 mole of a gas and let α be the fraction dissociated, then $(1-\alpha)$ mole remain undissociated. If 1 mole of a gas gives x moles of gaseous products on dissociation, α moles of the gas would give $x\,\alpha$ moles ; therefore, the total number of moles present at any time will be :

$$(1-\alpha) + x\,\alpha \text{ or } 1 + (x-1)\alpha.$$

Since the density of a given weight of gas at constant pressure is *inversely* proportional to number of moles, the ratio of density d_1, of undissociated gas to density d_2, of dissociated gas is :

$$\frac{d_1}{d_2} = \frac{1+(x-1)\alpha}{1} \qquad \therefore \quad \alpha = \frac{d_1-d_2}{d_2(x-1)}$$

When there is no dissociation, $\alpha = 0$ and $d_1 = d_2$; when dissociation is complete, $\alpha = 1$ and $d_1 = xd_2$; x is 2 for the following cases of dissociation :

$$NH_4Cl \rightleftharpoons NH_3 + HCl \; ; \quad PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

Substituting molecular weights for densities, $\alpha = \dfrac{m_1-m_2}{m_2(x-1)}$,

where m_1 = mol. wt. of undissociated gas, and m_2 = average mol. wt. of gases after dissociation.

Exercise.—(1) At 26°C vapour density of nitrogen peroxide is 38. Calculate the proportion of N_2O_4 molecules to NO_2 molecules in the vapour at this temperature. Vapour density of undissociated $N_2O_4 = 46$.

$$\begin{array}{cc} N_2O_4 \rightleftharpoons & 2NO_2 \\ 1-\alpha & 2\alpha \end{array}$$

$$\text{Degree of dissociation } \alpha = \frac{d_1-d_2}{d_2(x-1)} = \frac{46-38}{38} = 0.21$$

$$N_2O_4/NO_2 = (1-\alpha)/2\alpha = (1-0.21)/2\times0.21 = 1.88$$

(2) 4.5 g. of PCl_5 (mol. wt. 208.5) were completely vaporised at 250°C and the vapour occupied 1.7 litres at 1 atmosphere. Calculate degree of dissociation of PCl_5 at this temperature. *Calcutta B.Sc.*

$$PV = \frac{w}{m'}RT,$$

where $P = 1$ atmosphere, $V = 1.7$ litres. $R = 0.082$ litre-atmosphere

$T = 273 + 250 = 523°$ abs : m' = observed molecular weight.

$w = 4.5$ gm.

$$1\times1.7 = \frac{4.5\times0.082\times523.}{m'} \qquad \therefore \quad m' = 113.5$$

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$; α = degree of dissociation, and $x = 2$.

$$\frac{m-m'}{m'(x-1)} = \frac{208.5-113.5}{113.5} = 0.836$$

Exercises

1. State (a) Le Chatelier's principle, (b) Law of mass action and give one illustration for each, either in the laboratory or in industry.

2. What is meant by thermal dissociation ? How is it distinguished from electrolytic dissociation ? Give examples. Describe an experiment illustrating thermal dissociation.

3. Explain 'dissociation is a reversible reaction'. What is the effect of (a) temperature, (b) pressure, on the dissociation of (i) PCl_5 and (ii) HI ?
Ajmer Inter., 1932

4. By an experiment the vapour density of ammonium chloride is found to be 13.37. How would you explain the difference between observed and calculated value? Give experimental evidence in support of your explanation. *Punjab*, '28

5. What is meant by a reversible reaction? Illustrate your answer with reference to interaction between steam and iron. *Allahabad*, '13

6. Explain the difference between dissociation and decomposition. Illustrate your answer by reference to ammonium nitrate, ammonium chloride, calcium carbonate and potassium chlorate.

7. At 90°C vapour density of nitrogen peroxide N_2O_4 is 24.8 ($H = 1$). Calculate the degree of dissociation into NO_2 molecules at this temperature. *Ans.* 0.8547

8. When phosphorus pentachloride was vaporised at 20°C, its vapour density was found to be 70.0. Find the degree of dissociation of PCl_5 at this temperature. *Ans.* 0.4893

9. When 2 gm. of PCl_5 was vaporised in a vessel of 250 c.c. capacity at 250°C, the pressure developed was 3 atmospheres. What is the degree of dissociation of PCl_5 under these conditions? *Ans.* 82.2 per cent

10. Explain what you understand by reversible reaction. Discuss the effect of temperature and pressure on :

(a) $2SO_2 + O_2 \leftrightarrows 2SO_3$ (b) $3O_2 \leftrightarrows 2O_3$

(c) $N_2 + 3H_2 \leftrightarrows 2NH_3$ (d) $2NO_2 \leftrightarrows 2NO + O_2$

Bombay Inter., 1953

XI

ELECTROLYTES AND THE IONIC THEORY

Substances are grouped as conductor and non-conductor according as they conduct electric current or not. There are, again, two types of conductors :

(i) **Metallic conductors.**—Substances which conduct current without undergoing any permanent change are called *metallic conductors.* Electricity is carried by electrons in metallic conductors. All metals and a few substances which are not definitely metallic such as gas carbon and selenium, belong to this class.

(ii) **Electrolytes.**—Compounds which in *solution* or in the *fused state* conduct electric current and undergo simultaneous decomposition are called *electrolytes* ; electrolytes may be acids, bases and salts. Salts and alkalis which are bad conductors when solid, are excellent electrolytes when fused. Aqueous solutions of acids, bases and salts are also good electrolytes. Electricity is carried by ions in electrolytes.

Pure water is such a feeble electrolyte that it is often classed as a non-conductor. Mercury is a good conductor but not an electrolyte. Anhydrous hydrofluoric acid, alcohol, sugar solution, etc., are examples of a non-conductor.

Electrolysis.—When an electric current is passed into an aqueous solution of zinc chloride by dipping two platinum plates—one connected with the positive and the other to the negative pole of a battery—into the solution, decomposition occurs with the liberation of zinc and chlorine. The platinum plates leading the current in and out of the solution are called *electrodes*—the electrode connected to the positive pole of the battery is charged with positive electricity and is called the *anode*, and that connected with the negative pole of the battery is charged with negative electricity and is called the *cathode.*

The solution of the electrolyte zinc chloride undergoes reversible dissociation, yielding ions (electrically charged atoms or radicals) of opposite charges :

$$ZnCl_2 \rightleftharpoons Zn^{++} + 2Cl^-$$

The positively charged ions are called **cations** while the negatively charged ions are called **anions.** The cation, viz., the Zn^{++} ion, migrates to the cathode and gets discharged on its surface and becomes converted to a zinc atom. The anion, viz., Cl' ion moves to the anode and is discharged on its surface as an atom of chlorine—the atoms combine to form a molecule which is liberted as gas.

$$\text{At cathode } Zn^{++} + 2e = Zn\ ;$$

$$\text{At anode } Cl^- - e = Cl\ ;\ Cl + Cl = Cl_2.$$

where *e* represents a unit of negative charge called *electron.*

The electricity is, therefore, carried across from one electrode to the other by the ions, and hence the moving ions constitute the current in the electrolyte. Fused zinc chloride behaves similarly. *Such a process of conduction of an electric current by an electrolyte either fused or in solution, and the accompanying chemical decomposition* are called electrolysis.

Ions.—Ions are electrically charged atoms or radicals, (i.e., atoms or group of atoms which have gained or lost electrons, thus acquiring negative or positive charges, respectively) usually produced during the reversible dissociation of an electrolyte in its aqueous solution or in the fused state.

The electrolyte resolves into ions of opposite charges—the metals and hydrogen produce cations and the non-metals and acid radicals anions. The ions are the carriers of electric current in electrolysis. When an electric current is passed through an electrolyte the cations deposit at the cathode and are called *electro-positive groups* while the non-metals and acid radicals appear at the anode and are called *electro-negative groups.* Hence, *metals are electro-positive and non-metals electro-negative.*

$$H_2SO_4 \rightleftharpoons 2H^+ \text{ (cation)} + SO_4^{--} \text{ (anion).}$$

$$NaCl \rightleftharpoons Na^+ \text{ (cation)} + Cl^- \text{ (anion).}$$

$$Ca(NO_3)_2 \rightleftharpoons Ca^{++} \text{ (cation)} + 2NO_3^- \text{ (anion).}$$

The hydroxyl ion OH^-, is an anion, and is discharged at the anode during electrolysis. $NaOH \rightleftharpoons Na^+ + OH^-$

Theory of electrolytic dissociation.—To explain the phenomenon of electrolysis the Swedish chemist *Arrhenius* (1887) put forward the theory of electrolytic dissociation which states :

(i) The molecules of an electrolyte such as an acid, base or salt when dissolved in water, mostly split up or dissociate spontaneously into positively and negatively charged ions—the ions produced remaining in equilibrium with the undissociated molecules. This phenomenon is called **electrolytic dissociation,** and is *reversible* in character. Molecules of sodium chloride, sulphuric acid, copper sulphate, caustic soda, for example, dissociate in their aqueous solutions in the following way :

$$NaCl \rightleftharpoons Na^+ + Cl^- \; ; \qquad NaOH \rightleftharpoons Na^+ + OH^-$$

$$CuSO_4 \rightleftharpoons Cu^{++} + SO''_4 \; ; \qquad H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{=}$$

Since the solution as a whole is uncharged, the sum of the charges on the cations must be equal to the sum of the charges on the anions.

(ii) The degree of ionisation, i.e., the extent to which an electrolyte dissociates into ions, largely depends on such factors as dilution, temperature, presence of other ions in solution, and above all, on the nature of the electrolyte and the ionising medium. Many acids, bases and salts such as hydrochloric acid, caustic soda and common salt, show a very high degree of ionisation even at ordinary dilution, and are called **strong electrolytes,** whereas substances like acetic acid and carbonic acid ionise to a very small extent only and are known as **weak electrolytes.** The electrolytic dissociation, also called **ionisation,** steadily increases with dilution up to an '*infinite dilution*', i.e., up to a very great *dilution*, when the electrolyte *completely* splits into ions. Ionisation is practically complete in a very dilute solution. Ionisation is helped by rise of temperature.

(iii) It is the ions which conduct current during electrolysis—the undissociated molecules taking no part in the conduction. In general the greater the dilution or higher the temperature, the greater is the degree of ionisation and hence also the higher is the conductivity of the solution. The cations and the anions migrate to the cathode and the anode respectively ; and are discharged there.

It is useful to remember that *hydrogen and the metals are deposited at the cathode, and the acid radicals are liberated at the anode.*

According to Arrhenius's theory any reaction between electrolytes in solution is a *reaction between ions*—it is really the ions that interact. When silver nitrate is added to sodium chloride solution, a white precipitate of silver chloride is formed, since the silver ion reacts with the chloride ion forming insoluble silver chloride :

$$AgNO_3 \leftrightharpoons Ag^+ + NO_3' \; ; \qquad NaCl \leftrightharpoons Na^+ + Cl^-$$

$$Ag^+ + Cl^- \leftrightharpoons AgCl \; ; \qquad HCl \leftrightharpoons H^+ + Cl^-$$

$AgNO_3$ is the reagent for chloride ion, Cl' and precipitates it as silver chloride from an aqueous solution of a chloride, *independent of its cation ;* thus solutions of HCl, KCl, $CaCl_2$, etc., all give a precipitate with silver nitrate. Potassium chlorate, $KClO_3$, on the other hand, though it contains chlorine, gives no precipitate with silver nitrate, since on ionisation it yields chlorate ion, ClO_3' and *no chloride ion.*

$$KClO_3 \leftrightharpoons K^+ + ClO_3^-$$

Silver nitrate is a reagent for chloride ion and not for chlorine merely. Similarly, barium chloride is the reagent for sulphate ion and gives a precipitate of barium sulphate with sulphuric acid or its salt in solution.

$$H_2SO_4 \leftrightharpoons 2H^+ + SO_4'' ; \quad BaCl_2 \leftrightharpoons Ba^{++} + 2Cl^-$$

$$Ba^{++} + SO_4'' \leftrightharpoons BaSO_4$$

Illustrations of electrolysis.—(i) **Electrolysis of water.** Water is a *feeble* electrolyte, and only slightly dissociate into H^+ and OH^- ions : $H_2O \rightleftharpoons H^+ + OH'$. Its conductivity is increased by adding dilute sulphuric acid which dissociates greatly yielding H^+ and SO_4'' ions :

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4''.$$

During electrolysis using platinum electrodes the hydrion, H^+ is discharged at the cathode as an atom of hydrogen—the atoms form molecules which are evolved as gas : of the hydroxyl, OH', and the sulphate, SO_4'', ions, the hydroxyl ions, OH^-, are preferentially discharged at the anode—the OH radicals then react with one another forming water and evolving oxygen.

At cathode $\quad H^+ + e = H ; H + H = H_2$

At anode $\quad OH^- - e = OH ; 4OH = 2H_2O + O_2$

Same consideration applies to the electrolysis of dilute sulphuric acid.

(ii) **Electrolysis of sodium chloride.**—The aqueous solution of sodium chloride dissociates, yielding Na^+ and Cl' ions, and water furnishes H^+ and OH^- ions :

$$NaCl \rightleftharpoons Na^+ + Cl' ; H_2O \rightleftharpoons H^+ + OH^-$$

During electrolysis with *graphite electrodes* H^+ ions *and not the* Na^+ *ions* are preferentially discharged at the cathode, and the hydrogen is liberated as a gas. The chloride ions are discharged at the anode—the chlorine evolves as a gas at the anode.

At cathode $H^+ + e = H ; \; H + H = H_2$

At anode $\quad Cl^- - e = Cl ; \; Cl + Cl = Cl_2$

The solution after electrolysis, therefore, contains Na^+ and OH' ions, i.e., caustic soda, $NaOH \rightleftharpoons Na^+ + OH^-$

During electrolysis with *mercury cathode*, as in Castner-Kellner cell, the Na^+ ions, *and not the H^+ ions*, are preferentially discharged at the cathode—the liberated sodium dissolves in the mercury and forms an amalgam. The amalgam is then decomposed by water, giving caustic soda and hydrogen.

The chloride ions Cl^- are discharged, as usual, at the graphite anode, and the chlorine is liberated as a gas.

(iii) **Electrolysis of copper sulphate.**—Copper sulphate yields on ionisation, Cu^{++} and SO_4'' ions ; water yields H^+ and OH^- ions. Hence the solution contains these four ions.

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4'' ; \; H_2O \rightleftharpoons H^+ + OH'.$$

During electrolysis *at copper electrodes* copper ions are discharged at the cathode and liberated as a deposit of metallic copper, while at the anode copper atoms pass into solution as cupric ions Cu^{++}, —sulphate ions are not discharged since the negative charges are removed more easily from a copper atom than from a sulphate ion SO_4''.

At cathode $Cu^{++} + 2e = Cu$; At anode $Cu - 2e = Cu^{++}$

Hence, during electrolysis of copper sulphate, copper dissolves at the anode and deposits at the cathode.

During electrolysis *at platinum anodes*, cupric ions are discharged as usual at the cathode, while OH^- ions, *and not the SO_4'' ions*, are preferentially discharged at the anode—the OH groups then react to form water and oxygen which evolves as a gas.

During electrolysis the Cu^{++} ions and the OH^- ions are discharged, and consequently the solution contains the H^+ and SO_4'' ions, i.e., sulphuric acid after electrolysis.

(iv) **Electrolysis of caustic soda.**—The aqueous solution of caustic soda contains, H^+, OH^- and Na^+ ions ;

$$H_2O \rightleftharpoons H^+ + OH' \text{ ; } NaOH \rightleftharpoons Na^+ + OH'.$$

On electrolysis OH' ions are discharged at the anode—OH radicals react evolving oxygen, while the H^+ ions (and *not* Na^+ ions) are preferentially discharged at the cathode. Hence the electrolysis of caustic soda solution evolves hydrogen and oxygen only.

Ampere and Coulomb.—The practical unit of current, called the **ampere,** defined as the current which, flowing uniformly for 1 second, deposits 0.001118 gram of silver from a solution of silver nitrate. The unit quantity of electricity, called the **coulomb,** is the quantity of electricity passing when 1 ampere flows for 1 second. If q coulombs of electricity pass when c amperes flow for t seconds, then

$$q = c \times t$$
$$\text{Coulomb} = \text{ampere} \times \text{second}$$

Faraday's laws of electrolysis.—As a result of his investigations on electrolysis Michael Faraday in the year 1832 enunciated two laws indicating the relation between the quantity of electricity passing through an electrolyte and the amount of any substance liberated at the electrode.

First law.—*The weight of an ion deposited or formed at an electrode is directly proportional to the quantity of electricity passing through an electrolyte, i.e.,* $w \propto q$,

where w = weight in gram of the ion liberated by q coulombs of electricity when a uniform current of c amperes flow for t seconds.

$\therefore$ $q = c \times t$; but $w \propto q$; $\therefore$ $w \propto c \times t$; or $w = z \times c \times t$, when z is a constant and is called the *electrochemical equivalent.*

For the passage of same (q) quantity of electricity the weights (w_1 and w_2) of 2 ions deposited are proportional to their electro-chemical equivalents (z_1 and z_2).

$$w_1 = z_1q \text{ and } w_2 = z_2q \text{ ; } \therefore \; w_1/w_2 = z_1/z_2$$

Electrochemical equivalent.—When c = 1 ampere and t = 1 second, z becomes equal to w gms. Hence, *the electro-chemical equivalent* (*E. C. E.*) *of an element is its weight in grams which is liberated by the passage of one coulomb of electricity through the electrolyte, i.e.*, by a uniform current strength of one ampere flowing for one second. Thus 1 coulomb of electricity deposits from a solution of silver nitrate 0.001118 gram of silver, which is, therefore, the E.C.E. of silver.

The E. C. E. of hydrogen = 0.0000104.

The E. C. E. of silver = 0.001118 gm.

Second law.—*The weights of different ions deposited or formed at the electrodes, when the same quantity of electricity passes through different electrolytes are proportional to their chemical equivalents.*

Three electrolytic cells—the first one containing acidulated water, the second a solution of copper sulphate, the third fused stannous chloride—are connected in series so that same current passes through all of them. After electrolysis for some time, the volumes of hydrogen and oxygen liberated from the acidulated water, and the weights of copper and tin deposited from the copper sulphate solution and the fused stannous chloride respectively, are determined (fig. 48).

It is found that when 1.008 gm. of hydrogen is evolved, the weights of oxygen, copper and tin liberated are 8,31.78 and 59.3 gms. respectively—8,31.78 and 59.3 being the chemical equivalents of oxygen, copper and tin espectively. Hence the verification of the second law.

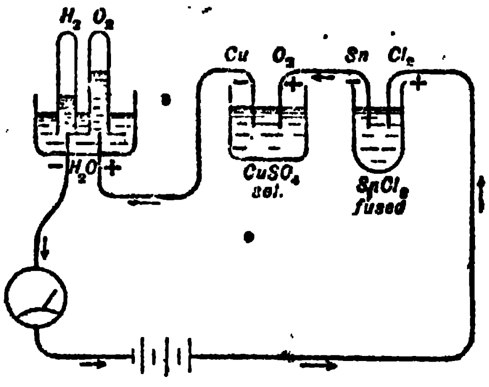


Fig. 48

Let w_1 and w_2 be the weights of two elements (of equivalent weights E_1 and E_2 respectively) deposited by the same quantity (q coulombs) of electricity. Then

$$w_1/w_2 = E_1/E_2$$

But according to the first law (w = zq), for the passage of the same (q coulombs) quantity of electricity the weights of ions liberated are proportional to their electrochemical equivalents, i.e.,

$$w_1/w_2 = z_1/z_2\ ; \quad \therefore \quad z_1/z_2 = E_1/E_2.$$

When one of the substances liberated is hydrogen for which E = 1.008, and z = 0.0000104, the relation becomes :

$$z/0.0000104 = E/1.008$$

$$\therefore \quad z = E \times 0.0000104/1.008$$

or electrochemical equivalent = chemical equivalent × 0.0000104 nearly.

Combination of Faraday's laws.—Since w ∝ ct (*first law*) and also w ∝ E (second law), the combination of the two laws of electrolysis leads to the relation :

$$w \propto ct\,E. \text{ or } w = ct\,E/F,$$

where 1/F is the proportionality constant.

Taking the quantity of electricity ct equal to F, w becomes equal to E, i.e., the weight of a substance deposited or dissolved is equal to the equivalent weight. Therefore, *F, called the* **faraday,** *is the quantity of electricity required to deposit or dissolve 1 gram equivalent of a substance in electrolysis.*

1 coulomb of electricity deposits 1 electro-chemical equivalent, i.e., 0.001118 gram, of silver in electrolysis. Therefore, the quantity of electricity required to deposit 1 gram equivalent, i.e., 107.88 grams, of silver, and hence 1 gram equivalent of any substance, is :

$107.88 \div 0.001118 = 96494$ coulombs, which is usually rounded off to 96500, i.e., $F = 96500$ coulombs

96500 *coulombs,* i.e., 1 *faraday of electricity,* therefore, *deposits or forms 1 gram equivalent of an ion in electrolysis.*

$$\therefore \quad w = \frac{ctE}{96500}$$

Significance of Faraday's laws.—1 gram equivalent of an ion carries 1 faraday of electricity.

$\therefore$ the quantity of electricity carried by 1 gram ion of valency n is nF coulomb, since 1 gram ion is numerically equal to 1 gram atom which is equal to gram equivalent × valency.

The number of individual ions in 1 gram ion is equal to the Avogadro number N which is 6.023×10^{23}, and the electric charge carried by a single ion is equal to nF/N. Since n is an integer, 1 for a univalent ion, 2 for a bivalent ion, and so on, the charge of electricity carried by a single ion is a multiple of the fundamental unit charge F/N. In other words, *electricity, like matter, is atomic in nature.* The unit of electric charge F/N has been identified with the charge of an *electron,* the unit negative charge.

When an atom loses one electron it forms a univalent cation which carries unit positive charge, e.g., Na^+, for which n is 1. The unit positive charge is equal but opposite to the unit negative charge, i.e., the electronic charge. A bivalent cation carries 2 unit positive charges and results from the loss of 2 electrons, e.g., Ca^{++}, for which n is 2. Similarly, an atom which has gained an electron forms a univalent anion which carries unit negative charge, e.g., Cl' ; a bivalent anion such as sulphate ion carries 2 unit negative charges, and so on. In general, *the electric charge carried by an ion is the same for all ions of the same valency and is proportional to the valency.* Therefore, the charge carried by an ion of valency n is ± ne, where e is the unit charge, and the charge on a gram ion is Nne, where N is the Avogadro number, and the charge on one gram equivalent is Ne. Hence $F = Ne$.

Determination of equivalent weight.—The equivalent weights of elements may be determined electro-chemically in two ways from the relations :

(i) $z = E \times 0.0000104/1.008$; (ii) $w_1/w_2 = E_1/E_2$.

(i) (a) **The equivalent weight of copper.**—The equivalent weight of copper may be determined by finding its electro-chemical equivalent in the following way.

The two copper electrodes of a copper voltameter which is a glass vessel only, are connected to the two terminals of a battery through an adjustable resistance and ammeter—the voltameter contains a solution of copper sulphate which has been acidified with a little sulphuric acid. The cathode which is a pure copper plate, is carefully cleaned, dried and weighed before the experiment, and then placed into the copper sulphate solution. A definite amount of current which is read from the ammeter, is sent through the copper sulphate solution for a given period of time.

After electrolysis, the cathode with a depoist of copper on it, is taken out, washed with distilled water, dried and weighed again—the difference in weight gives the weight of copper deposited. Suppose :

the copper deposited ... ... w grams.
the current passed ... ... c amperes.
the time ... ... t seconds.

$\therefore$ $w = zct$ or $z = w/ct$; where $z =$ electro chemical equivalent of copper.

Knowing z of Cu from $z = w/ct$, the E of Cu is determined from the relation : z of Cu = E of Cu $\times$ 0.0000104/1.008.

(b) **Electrochemical equivalent of silver.**—The electrochemical equivalent of silver is determined by passing electric current through a 30 p.c. solution of silver nitrate contained in a carefully weighed clean platinum crucible (*silver coulometer*) which forms the cathode. The anode is a rod of pure silver dipped into the solution in the crucible—a small glass cup is suspended under the anode to retain detached silver pieces. The crucible and the silver rod are connected to the terminals of a battery through a variable resistance and an ammeter. Current (c amperes) is passed for a given time (t seconds) when silver deposits on the platinum crucible. After electrolysis, the deposit is washed with water and alcohol, and the crucible is dried in an air-oven and weighed—let the weight of deposited silver be w grams.

From $w = zct$, $z = w/ct$.
Found $z = 0.001118$ gm. of silver.

This determination leads to the definition of ampere, the practical unit of current.

(ii) Two electrolytic cells, one containing copper sulphate solution and the other silver nitrate solution, are connected in series through an adjustable resistance and an ammeter. The same amount of electricity is sent through the two cells for a given time. The weights of copper and silver deposited on the respective cathodes are determined after electrolysis. Then by the second law of electrolysis.

$$\frac{\text{weight of Cu deposited}}{\text{weight of Ag deposited}} = \frac{\text{chemical equivalent of Cu}}{\text{chemical equivalent of Ag}}$$

Taking the chemical equivalent of silver to be 107.88, that of copper may be found out.

Dissociation.—There are many substances the molecules of which split up on heating into simpler molecules or atoms which, however, recombine on cooling—the phenomenon is called *dissociation*, or what is called *thermal dissociation.* The process of dissociation is *reversible* in character—the products of dissociation remain in equilibrium with the undissociated molecules.

Thus when ammonium chloride is heated, a fraction of its molecules dissociates into ammonia and hydrochloric acid which remain in equilibrium with the undissociated molecules of the ammonium chloride. $NH_4Cl \rightleftharpoons NH_3 + HCl$.

Calcium carbonate dissociates on heating into calcium oxide and carbon dioxide ; phosphorus pentachloride dissociates by heat into phosphorus trichloride and chlorine.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad CaCO_3 \rightleftharpoons CaO + CO_2$$

Iodine dissociates into atoms of iodine on heating : $I_2 \rightleftharpoons I + I$.

The thermal dissociation *differs* from ionisation in the following respects :

(i) Products of thermal dissociation are neutral atoms or molecules, while those of ionisation are electrically charged atoms or radicals, called ions.

(ii) Products of thermal dissociation are separable by physical means, such as solution, diffusion, etc., thus, the products of dissociation of ammonium chloride, ammonia and hydrochloric acid may be separated, partially though, by the process of diffusion, while the products of ionisation cannot be separated by such physical processes because of the existence of strong electrostatic attraction between the oppositely charged ions.

(iii) Thermal dissociation requires no medium, while in ionisaton the electrolyte is dissolved in an ionising solvent or is fused.

Both the processes are, however, *reversible* in character.

Decomposition.—The process ordinarily signifies the breaking up of a substance by heat into simpler substances which do not recombine on cooling and hence the process is *irreversible.*

Thus, ammonium nitrate decomposes by heat irreversibly into water and nitrous oxide ; potassium chlorate breaks up on heating into potassium chloride and oxygen.

$$NH_4NO_3 = N_2O + 2H_2O \; ; \; 2KClO_3 = 2KCl + 3O_2.$$

Technical Applications of Electricity.—Application of electricity in industries has virtually revolutionised production, but for it calcium carbide would have remained a laboratory curiosity, and aluminium a rare metal. Electro-chemical industries may be divided into several classes : (i) *fused electrolyte group* which involve *electrometallurgy* of sodium, potassium, calcium, magnesium, aluminium, etc., which are all obtained on a commercial scale by the electrolysis of fused compounds.

(ii) *those of an electrolytic nature,* further subdivided into group involving : (a) *electro-refining*—electrolytic copper, silver and nickel are examples. Copper will serve as an example. Anode is impure copper and pure copper is the cathode, while the electrolyte is a solution of copper sulphate in dilute sulphuric acid ; on electrolysis copper dissolves off the anode and is deposited on the cathode ; (b) *electro-separation*—production of alkali and chlorine by the electrolysis of brine, and the preparation of hydrogen and oxygen of very high purity by the electrolysis of alkalified water are the examples ; (c) *electrowinning*—copper is obtained by the leaching of the oxidised ore, brochantite, followed by electrolysis ; pure zinc is produced now-a-days by the electrolytic method ; (d) *electro-deposition,* represented by *electro-plating* and *electrotyping* mainly.

Electrotyping.—Books are printed from electrotype. A wax impression is first made of ordinary types, and is then covered with graphite powder to render the surface electrically conducting. This surface is copper plated by making it the cathode in an electrolytic cell where the anode is pure copper and the electrolyte copper sulphate solution. When a thick plate has been formed, it is detached from wax by melting off the latter. Printing is then done from the copper plate. Before used in printing, however, the plate is strengthened by backing with type metal. Similar process is employed for the reproduction of fine woodworks. Electro-blocks of diagrams, for example, are made from engraved wooden blocks.

Electroplating.—In electroplating a thin but a coherent film of a metal is deposited upon an article of another metal, which is made the cathode, by the electrolysis of a suitable salt solution. Usually articles of iron or brass are plated with nickel, copper, chromium, gold, etc., to prevent their corrosion and sometimes to add to their commercial value. Electroplating is done either for *protection against corrosion* or *decoration* alone or sometimes for both. Prior to plating, the articles are first treated with caustic soda solution to remove the greasy matter from the surface, and then with dilute hydrochloric or sulphuric acid to remove the oxide films. They are then washed and polished. The electrolytic bath consists of a solution of the salt of the plating metal—the cathode is the article to be plated and the anode the plating metal. In **nickel plating** nickel sulphate solution containing some boric acid is electrolysed between nickel-anode and the article to be plated as the cathode. In **silver plating** a solution of *potassium argentocyanide* is electrolysed, the anode being a plate of pure silver.

The electrolytic bath is prepared by adding excess of potassium cyanide to silver nitrate solution.

$$AgNO_3 + 2KCN = K[Ag(CN)_2] + KNO_3$$

$$K[Ag(CN)_2] \rightleftharpoons K^+ + [Ag(CN)_2]^- \; ; \quad [Ag(CN)_2]' \rightleftharpoons Ag^+ + 2CN^-$$

The anion, $Ag(CN)_2^-$ is only slightly dissociated—the silver ions are deposited on the cathode (articles to be plated) as a thin uniform film of metal instead of a coarse spongy deposit of silver when silver nitrate is used alone. The cyanide ions, CN^-, discharged on the silver anode, form silver cyanide which dissolves in excess of potassium cyanide forming potassium argentocyanide.

$$AgCN + KCN = K[Ag(CN)_2]$$

The electroplating bath in gold plating consists of a solution of potassium aurocyanide :

$$K[Au(CN)_2 \rightleftharpoons K^+ + [Au(CN)_2]^- \; ; \quad [Au(CN)_2]' \rightleftharpoons Au^+ + 2CN^-$$

As in silver plating, in **gold plating** as well gold dissolves from the anode and is deposited on the cathode. Table wares and jewellery are plated with gold or silver, Silver mirrors are plated with platinum to protect against tarnishing by atmospheric hydrogen sulphide. Iron is plated with zinc to guard against corrosion. Many metal fittings are plated with chromium or cadmium to preserve their polish.

(iii) *Electrolytic oxidation and reduction.*—Many important chemicals such as potassium permanganate, potassium persulphate, hydrogen peroxide, potassium chlorate, potassium percholrate and hydroxylamine, are obtained by this method.

(iv) *Group involving conversion of chemical to electrical energy,* as represented by secondary cells, e.g., lead accumulator.

(v) *Electrothermal group,* examples of which are white phosphorus, calcium carbide, graphite, synthetic abrasives like carborandum and alundum.

(vi) *Electric furnace products,* such as the ferroalloys, ferrochrome and ferromanganese, and the special steels like stainless steel, high speed tool steel, etc.

Applications in electrolytic industries apart, electrolysis offers excellent analytical methods for :

(i) *electrolytic estimation of metals,* e.g., copper, nickel, etc.,

(ii) *electroanalysis ;* for every metal there is a certain definite voltage at which it is deposited at the cathode. Hence it is possible to effect a separation of different metals by depositing them, only one at a time, at the cathode, by proper adjustment of voltage during the electrolysis of a solution of their salts in a mixture. Silver, for example, is deposited at lower voltage than cadmium, hence it is possible to separate silver from a mixture of the nitrates of silver and cadmium the decomposition potentials of the salts being $AgNO_3 = 0.70$ volt, and $Cd(NO_3)_2 = 1.98$ volts—when the applied potential is kept at a little less than 1 volt silver alone is deposited ; after the deposition of all the silver the current ceases. If the voltage is then raised to about 2 volts the cadmium is deposited.

(iii) *electrochemical equivalent and equivalents of metals.*

Electro-chemical Series.—It has been pointed out in connection with electrolysis that *metals and hydrogen are electro-positive*, i.e., they tend to lose negative electricity (electron) and form positive ions, while the *non-metals are electro-negative*, i.e., they tend to gain negative electricity (*electron*). This tendency to lose or gain electrons is measured by the E.M.F. that develops when an element is dipped into a normal solution of its ion. By means of such electro-chemical measurements elements have been arranged in an electro-chemical series, in which the metals are arranged in *descending order of electro-positiveness*, and the non-metals in *descending order of electro-negativeness.*

Electro positive elements

Potassium
Sodium
Barium
Strontium
Calcium
Magnesium
Aluminium
Chromium
Manganese
Zinc
Cadmium
Iron
Cobalt
Nickel
Tin
Lead
Hydrogen
Antimony
Bismuth
Arsenic
Copper
Mercury
Silver
Platinum
Gold

Electro-negative elements

Fluorine
Oxygen
Chlorine
Bromine
Iodine
Sulphur
Phosphorus
Nitrogen
Boron
Carbon
Silicon

The series which is an index of relative activities of the elements is a useful guide to the study of the properties of elements, thus :

(*i*) **Combination of metals with non-metals and radicals.**—A more electro-positive metal has greater affinity for a particular non-metal or radical than a less electro-positive of its salt ; e.g., iron displaces copper from a solution of copper sulphate ; sodium displaces aluminium from aluminium chloride.

$$Fe + CuSO_4 = FeSO_4 + Cu \; ; \; 3Na + AlCl_3 = 3NaCl + Al$$

Conversely, a more electro-negative non-metal will displace a less electro-negative non-metal from its combination with a metal e.g., chlorine displaces bromine from potassium bromide, while bromine displaces iodine from potassium iodide :

$$2KBr + Cl_2 = 2KCl + Br_2 \; ; \; 2KI + Br_2 = 2KBr + I_2$$

(ii) **Displacement of hydrogen from water and acids.**—Metals above hydrogen (with the exception of lead), displace hydrogen from hydrochloric or dilute sulphuric acids ; all the metals above hydrogen except lead and tin react with water liberating hydrogen—the higher the metal in the series the more vigorous the reaction ; e.g., potassium and sodium react violently with cold water and dilute acids ; brium, strontium and calcium react with less vigour under the same condition ; metals like magnesium and iron react with steam at high temperatures only.

$$2Na + 2H_2O = 2NaOH + H_2 \; ; \; Mg + H_2O = MgO + H_2.$$
$$Mg + 2HCl = MgCl_2 + H_2 \; ; \; Fe + H_2SO_4 = FeSO_4 + H_2.$$

Metals below hydrogen do not displace this element directly from water or dilute acids.

(iii) **Combination with oxygen.**—The stability of the metallic oxides increases with the increasing electro-positiveness of the metals ; e.g., the oxides of the metals above and up to aluminium are too stable to be reduced by carbon (magnesium excepted). The oxides of metals below aluminium are reduced by carbon with increasing ease with decreasing electro-positiveness of the metals. The stability of the oxides of mercury, silver and gold is so very low that they are decomposed by heat alone.

Acids, bases and salts.—Certain properties of acids and bases have already been mentioned (p. 36).

Acids are generally soluble in water—the solution has a sour taste, turns blue litmus red, and conducts electric current, since it dissociates into ions, *e.g.*,

$$HCl \rightleftharpoons H^+ + Cl^- ; \qquad H_2SO_4 \rightleftharpoons 2H^+ + SO_4''$$

Acids yield H^+ ions (also called, *protons*) on ionisation in aqueous solution ; hence *an acid may be defined as a hydrogen-containing compound which dissociates in aqueous solution with the formation of hydrogen ions as the only positive ion. An acid*, therefore, *may be defined as a proton donor.*

An alkali ionises in aqueous solution yielding the hydroxyl (OH') ions and no other negative ion, and conducts electric current.

$$NaOH \rightleftharpoons Na^+ + OH' ; \quad Ca(OH)_2 \rightleftharpoons Ca^{++} + 2OH'$$

A base may, therefore, be defined as a compound which, when dissolved on water undergoes dissociation with the formation of hydroxyl ions OH^- as the only negative ion.

Since the OH' ion of a base always reacts with H^+ ion of an acid producing water, *a base may be defined as a proton acceptor.*

Strength of acids and bases.—An acid in solution owes its acidic properties to the hydrogen ion it yields. Therefore the amount of H^+ ions formed by the ionisation (electrolytic dissociation) of an acid in aqueous solution may be taken as a measure of its strength—the greater the quantity of H^+ ions in the solution the stronger the acid. Hence acids which are highly dissociated in solution yielding large amount of H^+ ions are termed **strong acids,** while those which are but slightly dissociated are known as **weak acids.** The degree of dissociation is, therefore, a measure of the strength of an acid. The mineral acids HCl, HNO_3 and H_2SO_4 are strong acids, while the organic acids, oxalic acid and acetic acid are weak acids. Carbonic acid is a weak acid ; hydrocynic acid, HCN, is weaker still.

The concentration of OH' ions in solution is a measure of the strength of an alkali ; $NaOH$ and KOH are strong alkalis since they are largely ionised even in moderate dilution, while NH_4OH is a weak alkali.

The rate of solution of metals with evolution of hydrogen very clearly illustrates the strengths of acids. The order of strengths of the following three acids is $HCl > H_2SO_4 > CH_3COOH$ (acetic acid), as indicated by the volume of hydrogen evolved per minute from the dissolution of zinc in a definite volume, say, 100 c.c. of normal solutions of each of these acids.

Neutralisation.—When solutions of an acid and an alkali are mixed together in equivalent proportions the resulting solution has neither acid nor alkaline character—this reaction is called *neutralisation* which involves the formation of salt and water by interaction between the acid and the alkali :

$$NaOH + HCl = NaCl + H_2O$$

The acidic property of a solution is due to the presence of H^+ ions while the alkalinity is due to OH^- ions in a solution. Water is neutral since it contains H^+ and OH^- ions in equal amounts :

$$H_2O \rightleftharpoons H^+ + OH^-$$

When equivalent amounts of acids and alkalis are mixed together in aqueous solution, the H^+ ions of the acid react with the OH' ions of the alkali forming water—the process is called neutralisation and the solution is neutral, since it does neither contain H^+ nor OH^- ions in excess. Hence neutralisation is defined as a process which involves the formation of practically undissociated molecules of water from H^+ and OH^- ions of equivalent amounts of acids and alkalis respectively.

$$H^+ + Cl^- + Na^+ + OH^- \rightleftharpoons Na^+ + Cl^- + H_2O$$

$$i.e., \; H^+ + OH' \rightleftharpoons H_2O$$

Basicity of acids and acidity of bases.—Basicity of an acid is its power of neutralising a base and is measured by the number of replaceable hydrogen atoms in the molecule of an acid, i.e., by the number of hydrogen ions that one molecule of an acid can *give to a base* ; e.g., sulphuric acid H_2SO_4 is *dibasic*, since it can yield two H^+ ions in solution ; phosphoric acid H_3PO_4, is *tribasic ;* hydrochloric HCl and nitric acids HNO_3 are *monobasic.* Acids with one, two, and three replaceable hydrogen atoms are known as *monobasic* (or *monoprotic*), *dibasic* (or *diprotic*), *and tribasic* (or *triprotic*) acids respectively.

An acid is said to be **polybasic** (also called *polyprotic*) when a molecule of it yields more than one H^+ ion on ionisation ; a polybasic acid may ionise in stages :

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-. \quad HSO_4' \rightleftharpoons H^+ + SO_4''$$

Acidity of a base is its power of neutralising an acid and is measured by the number of replaceable hydrogen atoms of an acid with which a molecule of a base can react, i.e., by the number of hydrogen ions which one molecule of a base can accept from an acid. By this definition, caustic soda, NaOH, caustic potash, KOH and ammonia are *diacidic*, ferric hydroxide, $Fe(OH)_3$ *triacidic.* In the case of hydroxides the number of OH groups in a molecule represent its acidity.

Salts.—*A salt is a compound produced from an acid by the replacement of a part or whole of its replaceable hydrogen atoms by a metal or a basic radical.* A salt, therefore, consists of a metallic (or basic radical) linked to a non-metallic (or an acidic) radical. In zinc sulphate, for example, Zn is the basic radical and SO_4 the acidic radical ; in sodium nitrate Na is the basic radical and NO_3 the acidic radical. Salts dissociate into ions in solution :

$$ZnSO_4 \rightleftharpoons Zn^{++} \text{ (basic radical) } + SO_4'' \text{ (acidic radical).}$$

$$NaNO_3 \rightleftharpoons Na^+ \text{ (basic radical) } + NO_3' \text{ (acidic radical).}$$

Types of salts.—Three types of salts are distinguished.—(i) **Acid salts.**—Acid salts are formed by the partial replacement of the replaceable hydrogen atoms of a polybasic acid by a metal or ammonium and as such they contain some replaceable hydrogen atoms : hence an acid salt has the properties of salts in addition to those of acids. They are also known as **bisalts.** Examples are : sodium bicarbonate, $NaHCO_3$; sodium bisulphate (sodium hydrogen sulphate), $NaHSO_4$; disodium hydrogen phosphate, Na_2HPO_4. An acid salt is produced when a polybasic acid reacts with a quantity of a base insufficient to replace the whole of replaceable hydrogen atoms.

$$NaOH + H_2SO_4 = NaHSO_4 + H_2O.$$

$$NaOH + H_2CO_3 = NaHCO_3 + H_2O.$$

(ii) **Normal Salts.**—Normal salts are formed by the replacement of all the replaceable hydrogen atoms of an acid by a metal or ammonium. It thus contains neither the replaceable hydrogen atoms of an acid nor the oxygen or hydroxyl of a base. A normal salt is produced when equivalent amounts of acids and bases react :

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

$$2NaOH+H_2CO_3=Na_2CO_3+2H_2O \text{ ; } NaOH+HCl=NaCl + H_2O$$

Na_2SO_4, Na_2CO_3, $NaCl$—all are normal salts.

(iii) **Basic salts.**—Basic salts contain an excess of a base, i.e., oxygen or hydroxyl radical which may be replaced by acidic radicals forming normal salts. A basic salt is produced when a polyacid base is only partially neutralised by an acid.

$$Pb(OH)_2 + HCl = Pb(OH)Cl \text{ (basic lead chloride) } + H_2O.$$

White lead, $2PbCO_3$, $Pb(OH)_2$ and bismuth oxychloride, $BiOCl$, are basic salts. They are generally insoluble in water but dissolve in acids.

Bismuth oxychloride is produced as a white turbidity on diluting a solution of bismuth chloride with water—the turbidity, however, dissolves in the acid. $BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$.

Double Salts.—A double salt, such as potash alum, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$, is formed by the crystallisation of a solution containing the simple salts, potassium sulphate and aluminium sulphate, in molecular proportions. A double salt exists only *in the solid state*, but in solution it breaks up into the constituent simple salts and behaves in every respect as a *mixture of solution of these simple* salts—a double salt in solution, therefore, contains all the ions of the simple salts.

A double salt conforms to the law of constant proportions. Examples of double salts are ferrous ammonium sulphate, $(NH_4)_2SO_4$, $FeSO_4$, $6H_2O$, also called Mohr's salt, and carnallite, $KCl, MgCl_2, 6H_2O$.

Complex Salt.—A complex salt is a salt that contains one or more complex ions. A complex salt like potassium ferrocyanide, $K_4[Fe(CN)_6]$, is formed by adding excess of potassium cyanide to a solution of ferrous sulphate, until the precipitate of ferrous cyanide redissolves,

$$FeSO_4 + 2KCN = Fe(CN)_2 + K_2SO_4 \text{ ; } \quad Fe(CN)_2 + 4KCN = K_4[Fe(CN)_6]$$

and may be regarded as a mixture of ferrous cyanide and potassium cyanide in the proportion of one to four. But its solution does not give the reactions either of ferrous salts or of cyanides ; new properties appear which may be regarded as due to the formation of the complex ferro-cyanide ion, $Fe(CN)_6''''$, which does not break up in solution and has its distinctive reactions.

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]''''$$

A complex salt, therefore, is a distinct substance not only in the solid state, but, unlike a double salt, *retains its distinctive character even in solution.*

The complex ion may, however, partly dissociate in solution

$$K[Ag(CN)_2] \leftrightharpoons K^+ + [Ag(CN)_2]' ; \quad [Ag(CN)_2]' \leftrightharpoons Ag^+ + 2CN'$$

A complex salt conforms to the law of constant proportions like a double salt.

Hydrolysis of salts.—It might be expected that solutions of *normal salts* should be neutral in reaction, since they contain no replaceable hydrogen atoms nor any OH of a base. But this is true only in the case of *salts of strong acids and strong bases only ;* such salts simply ionise in solution :

$$NaCl \rightleftharpoons Na^+ + Cl^- ; \quad Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4''$$

Salts of weak acids or weak bases or both are *reversibly* split up by water with the formation of free acid and free base :

$$NaCN + HOH \rightleftharpoons NaOH + HCN$$

$$FeCl_3 + 3HOH \rightleftharpoons Fe(OH)_3 + 3HCl$$

and the process is called **hydrolysis**—the solution reacts *acidic* or *alkaline* according as the acid or base is relatively strong. Three cases of salt hydrolysis occur :

(i) **Salt of a weak acid and a strong base.**—Salts of weak acids (oxalic, acetic, carbonic, hydrocyanic, etc.) and strong bases (NaOH and KOH, etc.) are *alkaline* in reaction in their aqueous solution, since they are partially hydrolysed by water producing a *strong base* and a weak acid, e.g.

$$NaCN + HOH \rightleftharpoons NaOH + HCN \text{ (weak acid)}$$

$$Na_2CO_3 + 2HOH \rightleftharpoons 2NaOH + H_2CO_3 \text{ (weak acid).}$$

Solutions of sodium cyanide, NaCN, and sodium carbonate, therefore, react alkaline to litmus.

Owing to hydrolysis sodium carbonate behaves like a weak alkali in solution.

(ii) **Salt of a strong acid and a weak base.**—Salts of strong acids (HCl, HNO_3, H_2SO_4, etc.) and weak bases (metals like iron, aluminium, copper, etc., i.e., metals other than alkali metals, Na, K, etc. and the alkaline earth metals, Ba, Sr, Ca, etc., make weak bases) are all *acidic* in reaction in their solution, since they are partially split up by water producing a *strong* acid and a weak base, e.g.,

$$FeCl_3 + 3HOH \rightleftharpoons Fe(OH)_3 \text{ (weak base)} + 3HCl.$$

$$CuSO_4 + 2HOH \rightleftharpoons Cu(OH)_2 \text{ (weak base)} + H_2SO_4.$$

Aqueous solutions of ferric chloride and copper sulphate are, therefore, acidic to litmus.

(iii) **Salts of a weak acid and a weak base** is split by water into acid and base which are both weak—the solution may, therefore, be *neutral* when both are equally weak. Ammonium acetate solution is approximately neutral :

$$CH_3COONH_4 + HOH \rightleftharpoons CH_3COOH + NH_4OH$$

Ammonium formate solution reacts slightly acid, since ammonium hydroxide is weaker than formic acid.

$$HCOONH_4 + HOH \rightleftharpoons HCOOH + NH_4OH.$$

Hydrolysis may be explained as due to (i) the withdrawal of hydrogen ions from water, $H_2O \leftrightharpoons H^+ + OH^-$, by the anion of weak acid with the formation of a practically undissociated acid, leaving the hydroxide ions forming an alkaline reaction ; in the hydrolysis of sodium cyanide, NaCN, which is completely ionised in solution. $NaCN \leftrightharpoons Na^+ + CN^-$, the cyanide ions CN^- removes the hydrogen ions, H^+, from water, forming HCN which is practically undissociated, and the Na^- ions combines with the OH^- ions to form sodium hydroxide, which being a strong electrolyte, dissociates back into Na^+ and OH^- ions—the net result is the presence of hydroxide ions in solution and hence the alkaline reaction.

$$\begin{array}{ccc} NaCN \leftrightharpoons Na^+ & + & CN^- \\ H_2O \leftrightharpoons OH' & + & H^+ \\ \upharpoonleft\!\downharpoonright & & \upharpoonleft\!\downharpoonright \\ NaOH\text{ (highly ionised)} & & HCN\text{ (feebly ionised)} \end{array}$$

or (ii) the withdrawal of hydroxide ion of water by the cation of weak base, leaving excess of hydrogen ions to give an acid solution ; in the hydrolysis of ferric chloride the ferric ion withdraws the OH^- ions of water forming ferric hydroxide which is insoluble, and the chloride ions combine with the H^+ ions of water to form HCl which ionises back into H^+ and Cl' ions—hence the solutions contains H^+ ions and the solution reacts acid

$$\begin{array}{ccc} FeCl_3 \leftrightharpoons Fe^{+++} & + & 3Cl^- \\ 3H_2O \leftrightharpoons 3OH^- & + & 3H^+ \\ \upharpoonleft\!\downharpoonright & & \upharpoonleft\!\downharpoonright \\ Fe(OH)_3\text{ (insoluble)} & & 3HCl\text{ (highly ionised)} \end{array}$$

Acid salts possess the properties of salts in addition to those of acids but are not necessarily acidic in reaction. $NaHSO_4$, for example, is acidic to litmus, since it ionises yielding H^+ ions :

$$NaHSO_4 \rightleftharpoons Na^+ + HSO_4^- \; ; \; HSO_4^- \rightleftharpoons H^+ + SO_4''$$

Sodium bicarbonate, though an acid salt, reacts feebly alkaline to litmus in solution, owing to hydrolysis :

$$NaHCO_3 + HOH \rightleftharpoons H_2CO_3 + NaOH.$$

Preparation of acids.—The methods usually used include :

(i) The action of water upon acidic oxides ; e.g.

$$SO_3 + H_2O = H_2SO_4 \; ; \quad P_2O_5 + 3H_2O = 2H_3PO_4.$$

(ii) The action of water upon non-metallic halides—halides of non-metals are usually hydrolysed by water ; *CCl_4 is, however, stable towards water.*

$$PCl_3 + 3HOH = 3HCl + H_3PO_3 \text{ (phosphorous acid).}$$
$$SiCl_4 + 4HOH = 4HCl + H_4SiO_4 \text{ (ortho-silicic acid).}$$

(iii) The oxidation of non-metals.—Hot and concentrated nitric acid oxidises the non-metals carbon, sulphur, phosphorus, etc., to carbonic, sulphuric and phosphoric acids respectively, e.g.,

$$C + 4HNO_3 = CO_2 + 4NO_2 + 2H_2O$$
$$S + 2HNO_3 = H_2SO_4 + 2NO$$
$$4P + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2$$

(iv) Direct union of hydrogen with non-metals.—Hydrochloric acid is commercially obtained by this method. $H_2 + Cl_2 = 2HCl$.

(v) The action of an acid upon a salt.—A stronger acid displaces a weaker acid from its salt ; e.g.,

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$
$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

A less volatile acid, even if weaker, may displace a stronger but more volatile acid, e.g.,

$$NaCl+H_2SO_4 = NaHSO_4 + HCl,$$
$$NaNO_3+H_2SO_4 = NaHSO_4+HNO_3.$$

Sometimes the acids produced may separate as an insoluble precipitate ; e.g., $Na_2B_4O_7$ (borax) $+2HCl+5H_2O = 2NaCl+4H_3BO_3$.

Boric acid, H_3BO_3 being insoluble, crystallises out.

The acid produced may remain in solution, the salt of the reacting acid being thrown as a precipitate. The method is useful in preparing unstable acids : e.g.,

$$Ba(ClO_3)_2+H_2SO_4 = BaSO_4 + 2HClO_3 \text{ (chloric acid).}$$

Preparation of salts.—The methods usually employed include—

(i) The action of an acid upon a metal.—The method is often used for preparing chlorides, nitrates and sulphates : e.g.,

$$Fe+H_2SO_4 = FeSO_4+H_2 \; ; \quad Sn+2HCl = SnCl_2+H_2.$$

(ii) The action of an acid upon a base.—Soluble salts may be conveniently prepared by this method. The method also includes the reaction between basic and acidic oxides.

$$Al_2O_3+3H_2SO_4 = Al_2(SO_4)_3+3H_2O \; ; \quad ZnO+2HCl = ZnCl_2+H_2O$$
$$2NH_3+H_2SO_4 = (NH_4)_2SO_4. \quad Na_2O+SO_3 = Na_2SO_4.$$

(iii) The action of an acid upon a salt.—A stronger acid (HCl, HNO_3, H_2SO_4, etc.) displaces a weak acid (H_2CO_3, H_2S, etc.) from its salt—the salt of the stronger acid being produced ; e.g.,

$$CaCO_3+2HCl = CaCl_2+H_2O+CO_2 \; ; \quad FeS+H_2SO_4 = FeSO_4+H_2S.$$

A less volatile acid, even if weaker, may displace a stronger but more volatile acid from its salt ; e.g., $NaCl+H_2SO_4 = NaHSO_4+HCl$. *HCl is stronger than* H_2SO_4.

An insoluble salt may also be prepared by this method ; e.g.,

$$Pb(NO_3)_2+2HCl = 2HNO_3+PbCl_2 \text{ (insoluble).}$$
$$BaCl_2+H_2SO_4 = 2HCl+BaSO_4 \text{ (insoluble).}$$

(iv) Double decomposition of two salts.—Two salts in solution when mixed together may produce an insoluble salt by double decomposition ; e.g.,

$$AgNO_3+NaCl = AgCl \text{ (insoluble)} +NaNO_3.$$
$$Pb(NO_3)_2+Na_2SO_4 = PbSO_4 \text{ (insoluble)} +2NaNO_3.$$

(v) Direct union of the elements.—Many chlorides are prepared by passing chlorine over the heated metal ; e.g.,

$$2Fe+3Cl_2 = 2FeCl_3 \; ; \quad Sn+2Cl_2 = SnCl_4$$

Many sulphides may also be prepared by this method ; e.g.,

Mercuric sulphide, HgS, is prepared by simply grinding mercury and sulphur together ; $Hg+S = HgS$.

(vi) Displacement of the basic radical.—A more electro-positive metal displaces the less electro-positive one from its salt ; e.g.,

$$Fe+CuSO_4 = FeSO_4+Cu \; ; \quad Zn+2AgNO_3 = Zn(NO_3)_2+2Ag.$$

(vii) Oxidation or reduction of a salt.—Barium sulphide is prepared by reducing barium sulphate with coke ; zinc sulphide gives zinc sulphate on roasting in air ; e.g.,

$$BaSO_4+4C = BaS+4CO \;; \qquad ZnS+2O_2 = ZnSO_4.$$

Repression of ionisation by salt.—The ionisation of a weak acid or a base in solution is repressed by the addition of a salt having a common ion. Consider the ionisation of ammonium hydroxide.

$$NH_4OH \rightleftharpoons NH_4^+ + OH'$$

$$K \text{ (the ionisation constant)} = \frac{[NH_4^+]\,[OH']}{[NH_4OH]}$$

On adding NH_4Cl which ionises as $NH_4Cl \rightleftharpoons NH_4^+ + Cl'$, the concentration of NH_4^+ ion increase, and since K is constant, there must be an increase in the value of $[NH_4OH]$ and a decrease in the value of $[OH']$, i.e., some ammonium hydroxide formed, or in other words, the degree of dissociation of the ammonium hydroxide is reduced by the addition of ammonium chloride, with the consequent decrease in the concentration of OH^- ions.

• Similarly, the extent of ionisation of acetic acid is decreased by adding sodium acetate :

$$CH_3COOH \rightleftharpoons CH_3COO' + H^+ \;; \quad CH_3COONa \rightleftharpoons CH_3COO' + Na^+.$$

The degree of ionisation of the weak acid or base is inversely proportional to the concentration of the added salt.

Solubility product of an electrolyte.—The theory of electrolytic dissociation enables us to determine the conditions under which a substance either forms a precipitate or dissolves. Consider the equilibrium in a *saturated solution of sparingly soluble* silver chloride :

$$AgCl \text{ (solid)} \rightleftharpoons AgCl \text{ (dissolved)} \rightleftharpoons Ag^+ + Cl^-$$

$$\text{Applying law of mass action, } [Ag^+]\,[Cl^-] = K[AgCl]$$

The concentration of unionised solute in solution, [AgCl], is constant, since it is in equilibrium with *solid silver chloride* whose active mass is constnat. $\therefore$ $[Ag^+]\,[Cl^-] = S$ (a constant).

The constant S is called the solubility product for silver chloride. Hence, in a saturated solution of an electrolyte the product of concentration of the ions is constant.

The solubility product of an electrolyte *is the maximum product of the concentrations of the ions in its saturated solution at a given temperature.*

Common ion effect.—Sodium chloride is precipitated when HCl gas is passed into its saturated solution. The product of concentrations of Na^+ ions and Cl^- ions in the saturated solution of NaCl is constant :

$$[Na^+]\,[Cl^-] = \text{solubility product, S.}$$

The concentration of Cl^- ions is increased by passing HCl gas : $HCl \rightleftharpoons H^+ + Cl^-$; hence the concentration of Na^+ ions must decrease to keep the solubility product, S, constant. This occurs by the removal of some Na^+ ions from solution as solid sodium chloride, i.e., *some NaCl is precipitated*, until the product of the concentrations of ions reaches the solubility product. Hence the *solubility of an electrolyte is decrased by the presence of a common ion*—but, none the less, the solubility product remains constant. Silver chloride will, therefore, be less soluble in a solution containing silver nitrate or potassium chloride than in pure water.

Applications of solubility product.—

If, for a given electrolyte, the product of the concentration of ions in solution is made to exceed the solubility product, it is thrown out of solution as a precipitate ; if, on the other hand, the ionic product is made less than the solubility product, it passes into solution, that is, when :

product of ions$>$solubility product, the substance precipitates ;
product of ions$<$solubility product, the substance dissolves ;
product of ions $=$ solubility product, the solid substance remains in equilibrium with its saturated solution.

(i) **Precipitation.**—Consider the solubility product of the sulphides ; HgS, 4×10^{-54} ; CuS, 8×10^{-43} ; CdS, 5×10^{-29} ; ZnS, 1×10^{-20} ; MnS, 1.4×10^{-15}.

On passing hydrogen sulphide into a solution of salts of these metals, the metallic sulphide precipitates only when :

$$[M^{..}]\,[S'']>S, \text{ where } S = \text{solubility product}$$

and $M^{..}$ is the metal ion. Now, H_2S is a weak acid, and its dissociation :

$H_2S \leftrightharpoons 2H^{\cdot} + S''$, is readily suppressed by hydrogen ions.

When the solution is, therefore, acidified with dilute HCl ($HCl \leftrightharpoons H^{\cdot} + Cl'$), the concentration of sulphide ions, $[S'']$, is so much decreased that the solubility product of *very insoluble sulphides of group II metals*, e.g., HgS, CuS, CdS, etc., is only exceeded, and hence they are precipitated, whilst FeS, ZnS, MnS, etc, remain in solution.

The group III-A metals iron, aluminium and chromium are separated from zinc, managanese and magnesium by controlling the dissociation of the weak base ammonium hydroxide : $NH_4OH \leftrightharpoons NH_4^+ + OH^-$, by adding NH_4Cl which supplies the common ion, NH_4^+, by dissociation.

Ammonium chloride markedly represses the dissociation of ammonium hydroxide, thereby greatly lowering the concentration of OH^- ions. Hence when ammonium hydroxide is added to a solution of salts of these metals in presence of NH_4Cl, only hydroxides with low solubility products, e.g., $Fe(OH)_3$, $Al(OH)_3$, and $Cr(OH)_3$ are precipitated.

(ii) **Solubility of a precipitate.**—Consider a solid in contact with its saturated solution : MN (solid) $\leftrightharpoons$ MN (saturated solution) $\leftrightharpoons M^+ + N^-$
If either M^+ or N^- ions is removed, the equilibrium gets disturbed and more MN ionises and as a result the solution ceases to be saturated, and consequently more MN dissolves to restore the equilibrium. Therefore, any substance that removes M^+ or N^- ions helps the solution of MN.

Magnesium hydroxide which is but slightly soluble in water, readily dissolves in ammonium chloride solution. A suspension of magnesium hydroxide in solution forms a saturated solution for which the following conditions hold good.

$$Mg(OH)_2 \text{ (solid)} \leftrightharpoons Mg(OH)_2 \text{ (saturated solution)} \leftrightharpoons Mg^{++} + 2OH' \qquad \text{(i)}$$

$$[Mg^{++}]\,[OH']^2 = \text{solubility product of } Mg(OH)_2 \quad \ldots \quad \ldots \quad \text{(ii)}$$

On the addition of ammonium chloride ($NH_4Cl \leftrightharpoons NH_4^+ + Cl'$) the concentration of OH' ions is reduced by combination with NH_4^+ ions to form weakly ionised ammonium hydroxide which evolves ammonia,

$$NH_4^+ + OH' \leftrightharpoons NH_4OH \leftrightharpoons NH_3 + H_2O \quad \ldots \quad \ldots \quad \text{(iii)}$$

and the equilibrium (i) is thereby disturbed. In order to maintain the equilibrium by restoring the OH' ions that are removed, more magnesium hydroxide goes into solution and the process continues until all the magnesium hydroxide is dissolved. Owing to the continuous removal of OH' ions the ionic product, $[Mg^{++}]\,[OH']^2$, in the solution becomes less than the solubility product of magnesium hydroxide which, therefore, dissolves.

For similar reasons chalk dissolves in hydrochloric acid.

Silver chloride which has very little solubility in water, readily dissolves in aqueous ammonia. A suspension of silver chloride in water forms a saturated solution in which :

$$\text{AgCl (solid)} \rightleftharpoons \text{AgCl (saturated solution)} \rightleftharpoons Ag^{+} + Cl' \qquad \ldots \qquad \text{(i)}$$

and $[Ag^{+}]\,[Cl'] = \text{solubility product of AgCl} \qquad \ldots \quad \ldots \qquad \text{(ii)}$

On adding ammonia, the silver ion concentration is greatly reduced due to the formation of complex cation, $[Ag(NH_3)_2]^{+}$,

$$Ag^{+} + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^{+} \qquad \ldots \quad \ldots \qquad \text{(iii)}$$

and consequently, the ionic product, $[Ag^{+}]\,[Cl']$, in the solution falls below the solubility product of AgCl and hence it dissolves.

For similar reasons cupric hydroxide dissolves in ammonia—the cupric ions are removed due to the formation of the complex cation, $[Cu(NH_3)_4]^{++}$

$$Cu(OH)_2 \rightleftharpoons Cu^{++} + 2OH^{-} \,; \qquad Cu^{++} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{++}$$

Exercises

(1) The same amount of electricity which liberated 100 c.c. of oxygen collected over water at 15°C and 750 mm. of mercury, deposited 1.772 gm. of silver. Calculate the equivalent of silver, 1 c.c. of oxygen at N.T.P. weighs 0.001429 gm. Tension of aqueous vapour at 15°C = 13 mm.

$$\text{Volume at N.T.P. of oxygen liberated} = \frac{100 \times 273(750-13)}{28 \times 760} = 91.94 \text{ c.c.}$$

$$\text{Weight of oxygen} = 91.94 \times 0.001429 = 0.1314 \text{ gm.}$$

$$\frac{\text{Equivalent of Ag}}{8} = \frac{1.772}{0.1314}\,; \quad \text{Equivalent of Ag} = 107.9.$$

(2) Two cells, one containing copper sulphate and the other silver nitrate, were placed in the same circuit. It was found that 0.106 g. of Cu was deposited in the same time as 0.3597 g. of Ag. Calculate equivalent of silver and also find out the amount of silver which will be deposited when a current of 1.05 amperes is passed through the solution of silver nitrate for 20 minutes. Equivalent weight of copper = 31.8.
Calcutta 1953

$$\frac{\text{Equivalent of Ag}}{\text{Equivalent of Cu}} = \frac{\text{wt. of Ag deposited}}{\text{wt. of Cu deposited}}$$

$$\frac{\text{Equivalent of Ag}}{31.8} = \frac{0.3597}{0.106} \qquad \therefore \ \text{Equivalent of Ag} = 107.9.$$

$$\frac{\text{E.C.E. of Ag}}{\text{E.C.E. of } H_2} = \frac{\text{Eq. wt. of Ag}}{\text{Eq. wt. of } H_2}\,; \ \text{i.e.,}\ \frac{\text{E.C.E. of Ag}}{0.0000104} = \frac{107.9}{1.008}$$

$$\therefore \ \text{E.C.E. of Ag} = 0.001114,$$

$$\text{and wt. of Ag} = 0.001114 \times 1.05 \times 20 \times 60 = 1.404 \text{ gm.}$$

Alternatively from the relation w = Ect/96500.

$$w = 107.9 \times 1.05 \times 20 \times 60/96500 = 1.409 \text{ gm.}$$

(3) A current of 0.5 ampere is sent through a solution of copper sulphate for 20 minutes using platinum electrodes.

(i) Calculate weight of copper deposited at the cathode.

From the relation w = ct E/96500

$$\text{Weight of Cu} = \frac{0.5 \times 20 \times 60}{96500} \times \frac{63.57}{2} = 0.1977 \text{ g.}$$

(ii) Calculate number of copper atoms deposited.

1 gram atom, i.e., 63.57 gm. of Cu contain 6.023×10^{23} atoms.

$$\therefore \ 0.1977 \text{ g. of Cu contain } \frac{0.1977 \times 6.023 \times 10^{23}}{63.57} = 0.1873 \times 10^{23} \text{ atoms.}$$

(iii) Calculate volume of oxygen liberated at the anode at 27°C and 756mm.

$$\frac{\text{Wt. of } O_2 \text{ liberated}}{\text{Wt. of Cu deposited}} = \frac{\text{Eq. wt. of } O_2}{\text{Eq. wt. of Cu}}$$

∴ wt. of O_2 liberated = 0.1977×31.78 = 0.0497 g.

Volume of O_2 at N.T.P. = 0.0497×22400/32 = 34.79 c.c.

$$\therefore \text{ Volume at } 27°\text{C and } 756 \text{ mm} = \frac{34.79\times 760\times 300}{756\times 273} = 37.55 \text{ c.c.}$$

(4) The passage of a uniform current through dilute sulphuric acid with platinum electrodes for half an hour liberated 336 c.c. of electrolytic gas (mixed hydrogen and oxygen) at N.T.P. Calculate the strength of the current.

Volume of H_2 = 336×2/3 = 224 c.c. at N.T.P.
Volume of O_2 = 336×1/3 = 114 c.c. at N.T.P.
Weight of H_2 = 0.224×0.09 = 0.02 gm.
Weight of O_2 = 0.114×0.09×16 = 0.16 gm.
Applying w = ctE/96500,

$$- - \frac{\text{wt. of } H_2\times 96500}{30\times 60\times 1.008} = 1.072 \text{ amp.}$$

$$c = \frac{\text{wt. of } O_2\times 96500}{30\times 60\times 8} = 1.072 \text{ amp. ;}$$

Alternatively, 1 faraday i.e., 96500 coulombs simultaneously liberate 1 equivalent, i.e., 1 gm. or ½ mole of H_2 and 1 equivalent, i.e., 8 gm. or ¼ mole of O_2, making a total of ¾ mole of mixed gas per faraday. Volume of ¾ mole of gas at N.T.P. = 22.4×¾ = 16.8 litres. 16.8 litres of gases are liberated by 96500 coulombs.

∴ 0.336 litres of gases are liberated by 96500×0.336/16.8 = 1930 coulombs.

But coulomb = ampere×second.

∴ current strength = 1930/30×60 = 1.072 amp.

5. Explain and illustrate what you understand by electrolysis. State Faraday's laws of electrolysis and show how they may be verified experimentally. How would you determine the chemical equivalent of copper electro-chemically ?

6. What are the principal characteristics of electrolytic conduction ? How is the phenomenon explained by the hypothesis of ionic conduction ? Give a brief account of the hypothesis.

7. Write short notes on—(i) dissociation and decomposition ; (ii) electro-chemical equivalent. Deduce a relation between electro-chemical equivalent of an element and its chemical equivalent.

8. Give a short account of the ionic theory. Discuss in terms of the theory (a) strengths of acids and bases, (b) neutralisation, (c) hydrolysis.
Delhi Inter 1928

9. A current of electricity deposits 0.2 gm. of copper (eq. wt. 31.8) from copper sulphate solution in half an hour. What volume of oxygen could be obtained using acidulated water and a current twice as strong as in the former case for 2 hours ? If the gas were measured at 15°C and 765 mm. pressure, how would the result be altered ? 1 litre of oxygen at N.T.P. weighs 1.44 gm.
Ans. 279.6 c.c. ; 292.9 c.c.

10. An electric current is passed simultaneously through the following solutions ; hydrochloric acid, ferrous sulphate, ferric sulphate, and silver potassium cyanide. If 5.2 litres of hydrogen at N.T.P. were evolved from the hydrochloric acid solution how much metal would be deposited in the case of the iron and silver salts ? Fe = 56, Ag = 108. *Ans.* Iron 13.0, 8.7 gms. ; silver 50.1 gm.

11. Explain what is meant by electrolysis. Show how electrolysis may be used to find the equivalent of a metal. What meaning does the statement : *the E.C.E. of silver* is 0.001118 convey ? Explain with illustration the connection between valency and the charge of an ion.

12. Explain what is meant by a base. Is there any difference between a base and an alkali ? Would you consider sodium carbonate a base ?

13. Explain what is meant by salt, indicating its relation to (i) an acid, and (ii) a base. Describe the general methods for preparing salts. What is an *acid salt* ? Does an acid salt always have an acid reaction ? Give illustrations.

14. Explain what you understand by the terms acid, base and salt. What are their characteristic properties ? How are the salts classified ? Classify the following salts—sodium bicarbonate, copper chloride, sodium nitrate. Is the reaction of a salt always in keeping with its classifiction ? *Punjab* '37

15. Indicate briefly the theory underlying the process of neutralisation of an acid by a base. Solution of sodium carbonate and borax are alkaline to litmus, whilst solutions of copper sulphate and ferric chloride are acidic. Give reasons for this behaviour. *Calcutta* '39

16. An electric current is passed between platinum plates through solutions of copper sulphate, silver nitrate, and dilute sulphuric acid, the solutions being placed in series. If 0.105 gm. of copper is deposited in the first cell, calculate :—(a) the weight of silver separated from the second solution ; (b) the volume of hydrogen measured at 15°C and 740 mm. which is liberated from the third solution. Eq. wt. wt. of Cu 31.8, and that of Ag 108. *Ans.* (a) 0.3567 gm. ; 40 c.c.

17. A solution of a salt of a metal of atomic weight 112 was electrolysed for 150 minutes with a current of 0.15 ampere. The weight of metal deposited was 0.783 gm. Find the valence of the metal in the salt. *Ans.* 2

18. The same current is passed through acidulated water and through a solution of the chloride of metal X. The volume of hydrogen liberated at N.T.P. was 14.8 litres and the weight of metal deposited 42 gm. The specific heat of the metal is 0.094. Find the formula of the chloride. *Ans.* XCl_2

19. A current is passed for 6 minutes through a voltameter containing dilute H_2SO_4 liberated 40 c.c. of electrolytic gas, measured at 15°C and 748 mm. What was the average value of the current ? *Ans.* 0.596 amp.

20. In the preparation of NaOH by the electrolysis of a sodium chloride solution, 600 c.c. of solution containing 40 gms. NaOH per litre was obtained after a certain time. During the same time 30.4 grams of Cu (eq. wt. 31.8) had been deposited in a copper voltameter in series with the electrolytic cell. Calculate the percentage of theoretical yield of NaOH obtained. *Ans.* 62.75 per cent.

21. State Faraday's laws of electrolysis and explain the terms electrolyte and ions. What products are liberated at the electrodes or formed in the electrolyte during electrolysis : (a) dilute hydrochloric acid using carbon electrodes, (b) aqueous solution of sodium chloride using carbon electrodes, (c) solution of sodium sulphate using platinum electrodes ? *Punjab Inter*, 1944

22. What is the relation between : (a) electro-chemical equivalent and chemical equivalent of an element, (b) atomic weight and chemical equivalent of an element.? Calculate electro-chemical equivalent of silver and oxygen, given E.C.E. of H = 0.0000104, and Ag = 108, O = 16. *Bombay* '31
Ans. E.C.E. of Ag = 0.001114 ; E.C.E. of O = 0.00008254

23. An electric current is passed through solution of copper sulphate and cyanide of silver connected in series. If in a given time 0.35 g. of copper is deposited, what will be the weight of silver deposited in the same time ? Cu = 63.57, Ag = 107.8 *Punjab* 1945. *Ans.* 1.187 gm.

24. What is meant by salt hydrolysis ? Explain why an aqueous solution of sodium chloride is neutral towards litmus, a solution of sodium acetate is alkaline, and a solution of ferric chloride is acidic.

25. Explain the terms : (a) ion, (b) electro-chemical equivalent, (c) Faraday. *Calcutta* '53

26. State Faraday's laws of electrolysis and express them in the form of an equation. A current of 5 amperes is passed through a copper voltameter and a silver voltameter connected in series for 32 minutes and 10 seconds. Calculate the amount of Cu and Ag deposited. Given E.C.E. of Cu = 0.000325 g. and of Ag = 0.001118 g. *Calcutta* 1952, 1959. *Ans.* Cu 3.137 gm. ; Ag 10.79 gm.

27. Write a short note on the theory of ionisation. What is the difference between an atom and an ion ? How is the theory used to explain (a) neutralisation, (b) electrolysis, and (c) non-precipitation of zinc in group II during analysis. *Punjab* 1948

28. Explain the following on the basis of ionic theory : (a) use of ammonium chloride in qualitative analysis, (b) alkalinity of a solution of sodium carbonate and acidity of a solution of ferric chloride, (c) precipitation of pure sodium chloride from a saturated solution of the impure salt by HCl gas. *U. P. Board* '44

29. A current of 2 amperes was passed through a solution of copper sulphate for 16 minutes and 5 secs. Calculate the amount of copper deposited on cathode. Given 96500 coulombs can deposit 63.6/2 gms. of copper. *Cal.* 1959 ; 0.636 gm.

XII

THERMOCHEMISTRY

Thermochemistry is concerned with the evolution of heat that accompanies a chemical change. Heat is a form of energy and hence when a process is accompanied by a heat change, an equivalent amount of energy of some other from must be converted into heat. Heat is measured in calories. The *calorie* is the amount of heat required to raise the temperature of 1 gram of water through 1°C (from 15° to 16°C) ; 1 kilocalorie is equivalent to 1000 calories. 1 calorie (cal.) = 0.001 kilocalories (Cal.) = 4·1833 joules.

Heat of a reaction.—As stated before, vide page 15, chemical changes are accompanied by evolution or absorption of heat. Heat of a reaction is the quantity of heat evolved or absorbed during a chemical change. Reactions in which heat is evolved are *exothermic* reactions ; reactions in which heat is absorbed are *endothermic* reactions. Evolution of heat is taken as a positive (+) quantity and absorption of heat a negative (−) quantity in a thermo-chemical equation. Thus the equation :

$$C + O_2 = CO_2 + 97{,}000 \text{ cals.}$$

means the 97,000 cals are evolved in the formation of 1 gram molecule of CO_2. The equation : $C + 2S = CS_2 - 21{,}000$ cals. means that 21,000 cals. of heat are absorbed in the formation of 1 gram molecule of carbon disulphide, CS_2.

Intrinsic energy.—Under a given set of external conditions a substance contains a definite amount of energy, known as its *intrinsic* or *internal energy*. Consider the reaction :

$$C + O_2 = CO_2 + 97{,}000 \text{ cals.}$$

Heat of the reaction is +97,000 cals. Since no energy is lost in the transformation, intrinsic energies must balance on either side of the equation, when proper allowance is made for the heat evolved or absorbed in the process. It follows that :

$$\text{intrinsic energy of } C + \text{intrinsic energy of } O_2$$
$$= \text{intrinsic energy of } CO_2 + 97{,}000 \text{ calories.}$$

The internal energy of an element is not known, but since thermochemical measurements give only the *difference* of intrinsic energies of reactants and resultants, *the intrinsic energy of a free element in its normal state is arbitrarily taken as zero.* The intrinsic energy of CO_2 is then equal to −97,000 cals., meaning thereby that the intrinsic energy of a mole of CO_2 is 97,000 cals. *less* than its constituent elements.

Heat of formation.—Heat of formation of a compound is the amount of heat evolved or absorbed when 1 gram-molecule of the compound is formed from its elements in their normal state.

HF	+ 38, 500 cals.	H_2O	+ 68,300 cals.
HCl	+ 22,000 ,,	CO_2	+ 94,000 ,,
HBr	+ 8,440 ,,	CS_2	− 21,000 ,,
HI	− 6,400 ,,	NO	− 21,600 ,,

Heat of formation is a measure of the stability of a compound. The stability of the hydracids of halogens, for instance, progressively decrease from HF to HI.

Now, consider the reaction : $C + O_2 = CO_2 + 97{,}000$ cals.

Heat of formation of $CO_2 = +97{,}000$ cals., whereas the intrinsic energy of CO_2 is $-97{,}000$ cals, i.e., intrinsic energy of CO_2 is numerically equal to its heat of formation but is opposite in sign. Again, in the reaction $C + 2S = CS_2 - 21{,}000$ cals., heat of formation of CS_2 is $-21{,}000$ cals, but its intrinsic energy is $+21{,}000$ cals. In other words, *intrinsic energy = — heat of formation.*

Heat of combustion.—The heat evolved in the *complete* oxidation of 1 gram molecule of a substance (element or compound) is known as the heat of combustion.

The equation $C_2H_2 + 2\frac{1}{2}O_2 = 2CO_2 + H_2O + 310{,}615$ cals.

means that when 1 gram-molecule of acetylene is burnt in excess of oxygen 310,615 cals. of heat are evolved—this quantity is called the heat of combustion of acetylene.

Hess's law of constant heat summation.—The heat evolved in a chemical reaction is the same whether it takes place in one or several steps. Carbon, for example, may be burnt to CO_2 directly :

$C + O_2 = CO_2 + 97{,}000$ cals. Heat evolved $= + 97{,}000$ cals.

Now, carbon may be first combined with oxygen to give carbon monoxide and then CO may be burnt to CO_2 :

$$C + \tfrac{1}{2}O_2 = CO + x \text{ cals} \qquad \ldots \text{(i)}$$
$$CO + \tfrac{1}{2}O_2 = CO_2 + y \text{ cals.} \qquad \ldots \text{(ii)}$$

Heat evolved in the two steps (i) and (ii) must be equal to 97,000 cals., i.e., $x + y = 97{,}000$ calories.

Hess's law has been utilised to determine the heat of formation *indirectly*. In the above example heat of combustion of CO into CO_2 is $+ 68{,}000$ cals, hence $x + 68{,}000 = 97{,}000$, $\therefore$ $x = 29{,}000$ cals, i.e., heat of formation of CO is $+ 29{,}000$ calories.

Heat of solution.—Heat of solution of a substance is the amount of heat evolved or absorbed when 1 gram-molecule of the substance dissolves in such a large volume of water that further dilution causes no additional heat change. The solution is denoted by the symbol *aq.*, as HCl aq. Heat of solution of hydrochloric acid is 17,400 cals., and that of H_2SO_4 20,200 cals.

Heat of neutralisation.—This is the amount of heat liberated during the neutralisation of 1 gram equivalent of an acid by 1 gram equivalent of a base in their dilute solutions. Heat of neutralisation of a strong acid by a strong base is remarkably constant and is equal to 13,700 cals. Consider the neutralisation reaction :

$$HCl\ aq + NaOH\ aq = NaCl\ aq + H_2O + 13{,}700 \text{ cal.}$$

According to ionic theory, strong, acids and bases, and salts are completely ionised in their dilute solution, hence

$$H^+ + Cl^- + Na^+ + OH^- = Na^+ + Cl^- + H_2O + 13{,}700 \text{ cals.}$$

Disregarding the common ions on both sides of the equality sign,

$$H^+ + OH^- = H_2O + 13{,}700 \text{ cals.}$$

Hence, heat of neutralisation is nothing but the heat of formation of water from its ions. This is true for the neutralisation of equivalent amounts of any strong acid and strong base, and hence the constancy of the value.

$$KOH\ aq + HNO_3\ aq = KNO_3\ aq + H_2O + 13{,}700\ cals.$$
$$\text{or } K^+ + OH^- + H^+ + NO_3^- = K^+ + NO_3^- + H_2O + 13{,}700\ cals.$$
$$\text{i.e., } H^+ + OH' = H_2O + 13{,}700\ cals.$$

Exercises

1. What is meant by the heat of neutralisation of an acid ? Explain clearly why the heat of neutralisation of strong acids is approximately constant.
U. P. Board Inter., 1946

2. What are exothermic and endothermic reactions ? Explain with illustrations.

3. Write notes on : heat of formation, heat of neutralisation, heat of solution, and heat of combustion.

XIII

CATALYSIS

Catalysis.—In 1835, Berzelius drew attention to a number of reactions which were accelerated by the presence of an added substance which appeared to take no part in the reaction. This phenomenon he described as *catalysis*. Ostwald compared a catalyst to a lubricant which makes a machine move faster or to a whip which urges on a reluctant horse.

Catalysis is a process in which the rate of a chemical reaction is altered (either increased or decreased) by the addition of a small quantity of a foreign substance which remains unchanged in mass and chemical composition at the end of the reaction—the added substance is known as the catalyst.

Types of catalysis.—(a) **Positive catalysis.**—A catalyst may accelerate or retard the reaction. When a catalyst increases the rate of reaction, it is called a *positive catalyst*, and the process *positive catalysis* ; e.g., manganese dioxide acts as a positive catalyst in the decomposition of potassium chlorate into potassium chloride and oxygen ; finely divided platnium catalyses the reaction of hydrogen with oxygen to give water, and activated charcoal the reaction of hydrogen with chlorine to yield hydrochloric acid.

(b) **Negative catalysis.**—When a catalyst diminishes the rate of a reaction, it acts as a *negative catalyst*, and the process is *negative catalysis*, e.g., phosphoric acid acts as a negative catalyst in retarding the decomposition of hydrogen peroxide into water and oxygen. Glycerine retards the oxidation of sodium sulphite to sodium sulphate by air.

(c) **Autocatalysis.**—There are some reactions in which the products of the reaction act as catalysts ; this phenomenon is called *autocatalysis*. Thus, the declorisation of potassium permanganate in the titration of a hot solution of oxalic acid, in presence of sulphuric acid, is a very slow process at the start ; but the decolorisation is almost instantaneous as soon as a little manganous sulphate is formed, which catalyses the reaction.

(d) **Induced catalysis.**—A solution of sodium arsenite is not oxidised to arsenate on exposure to air, but sodium sulphite is oxidised to sulphate under the same condition. When a solution of a mixture of arsenite and sulphite is exposed to air, both salts are simultaneously oxidised. This is an example of *induced catalysis.*

$$Na_2SO_3+Na_3AsO_3+O_2 = Na_2SO_4+Na_3AsO_4$$

Characteristics of Catalytic Reactions :—(i) *The catalyst remains unchanged in mass and composition at the end of the reaction.* It may, however, undergo a physical change. Thus, coarse manganese dioxide added to catalyse the decomposition of potassium chlorate is found to be changed to very fine powder at the end of the reaction.

(ii) *A very small amount of the catalyst is only required.* Thus, a trace of copper sulphate at a concentration of only 10^{-12} gram molecules per litre markedly accelerates the rate of oxidation of sodium sulphite by air.

(iii) *A catalyst does not alter the position of equilibrium in a balanced action,* but only the velocity of reaction, and since a catalyst influences the forward and backward reactions to the same extent, it hastens up the quick attainment of the equilibrium state. Catalysts are usually used in exothermic reactions for the quick attainment of equilibrium at low temperatures at which these reactions are favoured.

(iv) *A catalyst cannot start a reaction but can only influence its rate.*

Experiments seem to contradict this statement, since there are many chemical changes which do not take place when the materials are *perfectly dry*—a trace of moisture being essential to start the reactions.

Thus, the combination of hydrogen and oxygen even in presence of finely divided platnium, and the union of nitric oxide and oxygen, do not take place in the complete absence of moisture. Perfectly dry carbon monoxide does not burn in dry oxygen. Sodium may be melted in dry chlorine without any chemical change, although they ordinarily interact vigorously even in the cold. Trace of moisture is thus a very active catalyst in many reactions.

Mechanism of Catalysis.—Catalytic reactions are grouped into two classes, namely, **homogeneous catalysis,** in which the catalyst is uniformly distributed throughout the system, i.e, all the substances concerned are in one phase, and **heterogeneous catalysis,** in which the catalyst, usually a finely divided solid, is not uniformly distributed throughout the system and forms a separate phase. Examples of homogeneous catalysis are (a) action of nitric oxide in the formation of sulphuric acid from sulphur dioxide, oxygen and water vapour, (b) influence of moisture in the formation of ammonium chloride from ammonia and hydrogen chloride, and (c) effect of acids in the hydrolysis of cane sugar to glucose and fructose. Examples of heterogeneous catalysis are found in most technical gas reactions, e.g., platinised asbestos is an effective catalyst in the oxidation of sulphur dioxide to sulphur trioxide in the contact process for sulphuric acid ; iron is a catalyst in the synthesis of ammonia in Haber's process ; active charcoal helps the formation of phosgene, $COCl_2$, from carbon monoxide and chlorine.

There are two theories to explain catalytic changes.

The "intermediate compound" theory, applicable to homogeneous catalysis, postulates that the catalyst combines with one of the reactants to form a *more reactive unstable* intermediate compound, which then reacts with other reactants to yield the products, simultaneously releasing the catalyst. The catalytic action of nitric oxide in the oxidation of SO_2 in the chamber process for sulphuric acid offers an example. Nitric oxide combines with atmospheric oxygen to form nitrogen peroxide, which then converts the sulphur dioxide to the trioxide—the nitric oxide that is set free again takes part in the reaction.

$$2NO + O_2 = 2NO_2 ;\quad 2SO_2 + 2NO_2 = 2SO_3 + 2NO$$

The adsorption theory, applicable to heterogeneous catalysis only, postulates that the reacting gases are adsorbed on the surface of a solid catalyst—the adsorbed layer is limited to a thickness of one molecule. The increase in the velocity of the reaction is attributed to the close proximity of the reactants in the adsorbed films. The product is formed on the surface and subsequently fly off, leaving the surface bare for fresh adsorption. The degree of adsorption and the catalytic activity increases with the fineness of sub-division of the catalyst.

Catalyst poisons and promoters.—The activity of a heterogeneous catalyst is sometimes appreciably altered by traces of foreign substances. Foreign substances which tend to inhibit catalytic activity are known as *anti-catalysts* or *catalyst poisons ;* they are more firmly and preferentially adsorbed than the reactants at the surface of a solid catalyst, which is thereby rendered ineffective. Thus, in the manufacture of sulphuric acid by the contact process, traces of arsenious oxide completely destroys the catalytic activity of platinum catalyst.

Substances which tend to enhance the activity of a catalyst are known as *promoters.* In the Haber process for the synthesis of ammonia with iron catalyst, for example, the addition of a trace of molybdenum produces a large increase in catalytic activity.

Industrial applications of catalysts.—Mention is made of few processes only.—

(a) *Synthesis of ammonia.*—Reduced iron with molybdenum as promoter is the catalyst in the synthesis of ammonia from its elements in Haber process.

(b) *Hydrogenation of oils and fats.*—Finely-divided nickel promotes addition of hydrogen to unsaturated compounds, and is used for the hydrogenation (hardening) of unsaturated fats and oils—the solid products being used for margarine.

(c) *Synthesis of hydrochloric acid from its* elements in presence of active charcoal.

(d) *Nitric acid.*—Platinum gauze is the catalyst in the oxidation of ammonia to nitric acid in Ostwald process.

(e) *Sulphuric acid.*—In the contact process platinised asbestos or vanadium pentoxide is the catalyst in the oxidation of sulphur dioxide to the trioxide.

Catalysis by enzymes.—Many chemical reactions are catalysed by complex organic substances called *enzymes* produced by living cells. Thus, the enzyme *invertase,* which occurs in yeast cells, hydrolyses cane-sugar to a mixture of glucose and fructose.

$$C_{12}H_{22}O_{11} \text{ (cane-sugar)} + H_2O = C_6H_{12}O_6 \text{ (glucose)} + C_6H_{12}O_6 \text{ (fructose)},$$

which, under the influence of the enzyme *zymase,* also present in yeast, are converted into ethyl alcohol and carbon dioxide.

$$C_6H_{12}O_6 = 2C_2H_5OH \text{ (ethyl alcohol)} + 2CO_2.$$

Exercises

1. Write an essay on catalysis and point out its importance in some industrial processes. *U. P. Board Inter.,* 1951

2. Write a short note on catalysis and its applications.

XIV

COLLOIDAL SOLUTIONS

The Colloidal State.—In course of his investigations on diffusion of solutions of various substances, Thomas Graham (1852-60) observed that acids, bases and salts could readily diffuse in solution and fairly quickly pass through vegetable and animal membranes, whereas substances like glue, starch and albumen diffused but very slowly. The rapidly diffusing substances were called by Graham **crystalloids** since most of them were crystalline in the solid state. Albumen starch, gum, proteins, etc., on the other hand, which form amorphous solid masses resembling glue, were called **colloids** from the Greek word *kolla*, meaning glue, which was a typical member of the group of substances that diffused very slowly. Graham thus differentiated between "two classes of matter, the crystalloid and the colloid," each with characteristic properties.

But in the light of later researches it is more correct to speak of the *colloidal state of matter* than to describe a substance as a colloid or crystalloid, since most substances may be obtained in the colloidal state under suitable conditions. Common salt, for example, which is a typical crystalloid in aqueous solution, may be brought into a colloidal state in benzene ; soap, which forms a colloidal solution in water, behaves as a crystalloid in alcoholic solution. It is the *size of the particle* which decides if a substance will remain in the colloidal state. The term colloid, therefore, refers not so much to a class of substance as to a *state of subdivision.*

In a true solution, such as one of common salt or sugar in water, the solute distributes in the solvent as ions or single molecules. A suspension, on the other hand, contains particles which are visible to the naked eye or, at least, in a microscope. Between these two extremes exists the *colloidal system in which the particles are larger than molecules but are not large enough to be seen under the microscope.* A coarse suspension, a colloidal solution and a true solution differ as regards *size of particles only. Size of particles :*

Coarse suspension	Colloidal particle	Molecular diameter
10^{-4} cm	10^{-5} to 10^{-7} cm	10^{-8} cm

9 **Dialysis.**—Colloids may be separated from crystalloids by a process, called dialysis. *Dialysis is a process of separation of a colloid from a crystalloid from a mixture of the two in solution by diffusion through a membrane, such as parchment paper and collodion film, which lets through the crystalloid but not the colloid.*

By means of dialysis a colloid is freed from crystalloidal impurities.

Experiment.—A solution of starch and potassium iodide is taken in a bell jar, over the mouth of which a piece of parchment paper is tightly tied—the apparatus is called a **dialyser** (fig. 49). It is suspended in a jar of distilled water, so that the parchment paper dips into the water. After sometime, about half an hour, chlorine water is added to the water in the water jar—a *yellow colour* due to liberated iodine shows that the crystalloid potassium iodide has passed through the parchment paper, but the starch is retained, which would, otherwise, have given a blue colour with the iodine ; on adding both chlorine water and starch into outer jar, blue colour develops, showing that potassium iodide alone did diffuse out.

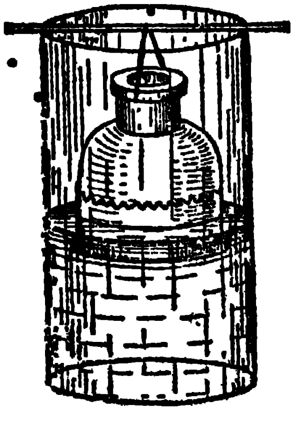


Fig. 49

Colloidal solution.—Unlike a true solution which is homogeneous, *a colloidal solution is heterogeneous* and consists of two phases, one of which is distributed throughout the other as small particles or droplets ; the substance that is in the form of particles or droplets is in the *colloidal state* and is known as the *dispersed phase*, and the medium in which the particles are distributed (or dispersed) is called the *dispersion medium*.

The dispersed phase and the dispersion medium may be solid, liquid or gas, except that two gases cannot form a colloidal system. When the dispersion medium is a liquid, the colloidal systems are called *sols* ; sometimes the sols are as thick as as jelly and are called *gels*. *Smoke* and *dust* consist of solid particles dispersed in a gaseous medium, whereas in *fog*, *mist* and *cloud* a liquid is dispersed in a gas. A *foam* consists of a gas dispersed in a liquid ; one liquid is dispersed as droplets in another liquid in an *emulsion*, e.g., milk is an emulsion of fat in water ; when a solid of relatively large particle size is distributed in a liquid the result is a *suspension*.

Classification and preparation of colloidal solution.—Colloidal solutions are roughly divided into two classes : **lyophilic** (solvent-loving), and **lyophobic** (solvent-hating). The dispersed phase exhibits great affinity for the dispersion medium in a lyophilic colloidal system, and consequently many substances forming lyophilic sols, readily pass into colloidal solution, when simply treated with a suitable dispersing medium, e.g., colloidal solutions of starch and gelatin in water, and rubber in benzene. On evaporation or cooling of lyophilic sols, solids are obtained which can be reconverted into sols by adding solvent or by warming, respectively. *Lyophilic sols are*, thus, *reversible in character*.

Many aqueous lyophilic colloidal sols occur naturally, e.g., starch, gelatin, rubber latex and egg albumen. Lyophilic silicic acid sol can be prepared artificially by pouring a dilute solution of sodium silicate into excess of dilute hydrochloric acid :

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3$$

Silicic acid is in the colloidal state. The sodium chloride and excess acid are removed from the sol by dialysis. Lyophilic colloid particles are heavily solvated.

The dispersed phase has no affinity for the dispersion medium in a lyophobic colloidal system. Lyophobic sols are, therefore, prepared by special methods, referred to as *condensation method* and *dispersion method*.

Condensation method.—Particles of colloidal size are obtained by this method as a result of chemical reaction between substances which are originally present in true solutions, as ions or molecules. Chemical reactions used are : (i) *Hydrolysis.*—Deep red ferric hydroxide sol is obtained by adding drop by drop ferric chloride solution to boiling water—the excess ferric chloride and the hydrochloric acid are removed by dialysis :

$$FeCl_3 + 3H_2O \leftrightharpoons Fe(OH)_3 + 3HCl.$$

(ii) *Metathesis.*—Yellow arsenious sulphide sol is prepared by passing H_2S into a solution of arsenious oxide in water—the excess H_2S is removed by bubbling hydrogen through the sol : $As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$.

(iii) *Oxidation.*—An aqueous solution of H_2S can be oxidised by sulphur dioxide to yield a sulphur sol : $SO_2 + 2H_2S = 3S + 2H_2O$.

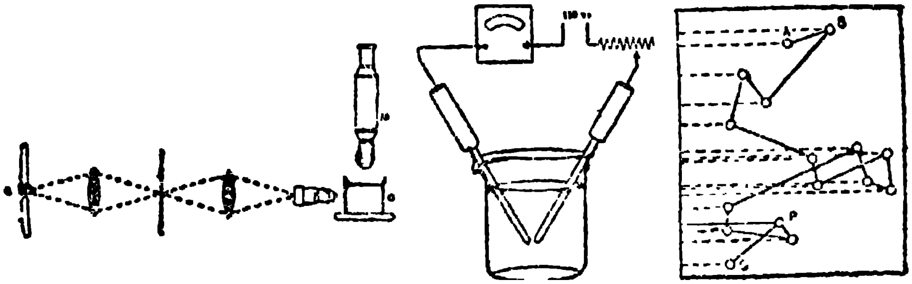
(iv) *Reduction.*—Metal sols (sols of Au, Ag and Pt, etc.) are obtained by the reduction of solutions of their salts with formaldehyde, hydroxylamine and hydrazine, etc. Zsigmondy's gold sol is prepared by reducing a solution of auric chloride with formaldehyde—the sol is ruby-red in colour when gold particles are fine, and blue with coarser particles.

Dispersion method.—By this method the material is disintegrated from the massive form into particles of colloidal size.

(i) *Mechanical dispersion.*—This is done in a *colloid mill* which consists of two closely spaced discs, rotating at a high speed in opposite directions. A mixture of the material to be dispersed and the dispersion medium (e.g., clay suspensions in water) is fed between the plates, where the shearing force produces particles of colloidal size.

(ii) *Peptisation.*—The term refers to the dispersion of a substance into particles of colloidal size by an added agent, known as a *peptising agent.* The presence of a common ion in small amounts helps peptisation. A precipitate of aluminium hydroxide passes into colloidal solution if shaken with water containing a little aluminium chloride. A dilute solution of $AgNO_3$ or KCl can peptise freshly precipitated AgCl to yield a colloidal sol.

Bredig's method which involves both dispersion and condensation makes use of *electrical disintegration.* Metal sols are prepared by this method, e.g., sols of Au, Ag, Cu, Pt., etc. A direct current electric arc is struck between two metal electrodes (fig. 50*a*) held under water, and the metal sol is formed. The metal is vaporised by the arc and the vapour is condensed by cold water to form colloidal particles.



(*c*) Fig. 50 (*a*) (*b*)

Once the dispersed phase is precipitated out from a lyophobic, sol, it can not be reconverted into the sol easily ; *lyophobic sols* are, therefore, called *irreversible sols.*

Properties of sols.—(i) **Diffusion and dialysis.**—The rate of diffusion of a sol is very much less than that of a solute in true solution. The process of purifying a sol from true solution, known as *dialysis*, depends largely on the differential rates of diffusion.

(ii) **Osmotic pressure.**—The osmotic pressures of colloidal solutions are very small. The very low osmotic pressures of sols distinguish them from true solutions.

(iii) **Optical properties.**—(a) **Tyndall effect.**—Colloidal particles are too small to be seen in a microscope. But just as dust particles in the path of light, when a sun beam enters a dark room, become visible due to scattering of light from their surface, so also when a strong beam of light is passed through a sol in a darkened room (fig. 50c), the individual colloidal particles scatter light and as a result they appear as flashes of light which can be observed and counted under a *ultra-microscope*, first constructed and used by Zsigmondy. The colloidal solutions, thus, scatter light, producing what is called Tyndall effect. A true solution does not show Tyndall effect and is said to be optically void.

(b) **Brownian movement.**—When observed in the ultra-microscope colloidal particles are found to undergo a ceaseless random motion, referred to as Brownian movement after the name of English botanist Robert Brown who in 1827, first observed this movement in pollen grains dispersed in water. The Brownian motion is due to the impact of the molecules of the medium on the colloidal particles (fig. 50b).

The Tyndall effect and Brownian motion are characteristics of colloidal solutions only.

(iv) **Electrical properties.**—(a) **Electrophoresis and electro-osmosis.** When a sol is placed in an electric field, colloidal particles move in one direction or another, showing that *the colloidal particles are electrically charged with respect to the dispersion medium.* When two platinum wires connected to the terminals of a battery, for example, are dipped in arsenic sulphide sol in a U-tube, the colloidal particles slowly move towards the positive pole, showing that they carry negative charges. This phenomenon of movement of colloidal particles under the influence of an electrical potential is called *electrophoresis ;* also called *cataphoresis.*

Colloidal particles of clay, arsenious sulphide, silicic acid and metals such as Au, Ag and Pt, carry negative charges, whereas haemoglobin, and metallic hydroxides, e.g., $Fe(OH)_3$ and $Al(OH)_3$, etc. are positively charged.

When an electric field is applied to a sol under condition in which the colloid particles are held stationary the liquid is observed to move—this effect is known as *electro-osmosis ;* when the colloid particles are negatively charged, the liquid moves towards the negative pole.

(b) **Coagulation of colloids.**—Electrical charge is an important factor in the stabilisation of colloids. When an electrolyte is added to a colloidal sol, the latter slowly gets turbid and finally the dispersed phases separates out as a precipitate ; this phenomenon is known as *precipitation or coagulation.* Coagulation is due to the neutralisation of the charge on the colloid particles by the oppositely charged ions of the added electrolyte. The coagulating power of an electrolyte depends upon the valency of its ions. **Hardy—Schulze rule** states that (i) *the ion which is effective in causing coagulation of a sol is the ion whose charge is of opposite sign to that of colloidal particles,* and (ii) *the coagulating power increases with increasing valency of the ion.* Bivalent sulphate ions, for example, are about 50 times more effective than univalent chloride or nitrate ions in coagulating positively charged ferric hydroxide sol. Charged colloids are also effective in coagulating colloids of opposite charge ; when positive ferric hydroxide sol and negative arsenious sulphide sol are mixed, mutual coagulation of two colloids take place. Heating a sol also favours coagulation. Lyophobic sols are relatively unstable compared with lyophilic sol ; the former is coaguated by small quantity of electrolytes but the latter is not affected unless large amounts of electrolytes are added. The addition of a lyophilic colloid to a lyophobic sol renders the latter less sensitive to coagulating effect of electrolytes. When this occurs the lyophobic sol is said to be *protected* and the lyophilic colloid is called a **protective colloid.** Gelatin, gum, albumen, etc., usually act as protective colloids. Graphite sols are protected by the addition of tannin ; gum-arabic acts as a protective colloid to ink preparations.

The phenomena of electrophoresis and electro-osmosis, and coagulation are characteristics of sols only.

Applications of Colloids.—Colloids play an important role in our everyday life and industry. Many of the substances composing the body of living organisms—the protoplasm itself—are colloids. Mention is made of few of its applications to focus its importance in science and technology :

(i) *Food.*—Many of our foods are colloids. Milk, for example, is an emulsion of butter-fat in water, stabilised by casein as an emulsifying agent. In ice cream the casein of milk and ice particles are in the colloidal state, stabilised by the presence of gelatin or albumen. Artificial beverages are mostly colloidal solutions or emulsions ; tea is a colloidal solution, coffee an emulsion.

(ii) *Medicines.*—Many pharmaceutical preparations are either emulsions or colloidal suspensions, e.g., cod liver oil emulsion, colloidal gold sol. Colloidal silver (*protargol* and *collargol*) is used in eye treatment.

(iii) *Vegetable tanning.*—Process of tanning is regarded as a union of tannins with hide fibre. Tannins dissolve in water forming colloidal sols, in which the particles are negatively charged. Hides soak water and swell forming a gel of positively charged colloid particles of collagen, the principal constituent of hide fibre. On mixing the two, hide and tannin, electrical neutralisation with the resulting coagulation of two colloids follow—this is the fundamental action in leather tanning.

(iv) *Formation of delta.*—Many rivers carry colloidal suspensions of clay particles which are negatively charged. When such a river reaches the sea, the salt concentration is high enough to bring about the coagulation of the clay particles which are deposited to form a delta—in this way new land, e.g., Gangetic delta, is continuously added at the mouth of the river.

(v) *Dust precipitation.*—Smoke, dust, mist, and fog, etc., are all colloidal suspensions of solids or liquids in gases, in which the individual particles are electrically charged. They can be deposited by Cottrell precipitator which consist of two metallic plates across which a very high potential, about 50,000 volts, is applied and between which the gas containing the dust, smoke, etc., is passed. Dust particles, etc., are attracted towards the plates of charge opposite their own and are discharged, and finally settle down, and the cleaned gas passes on. Cottrell precipitator is now an adjunct of many factories for the elimination of dust and mist, e.g., sulphuric acid concentration units, cement factories, and furnaces for smelting arsenical ores.

(vi) *Cleansing action of soap.*—Soap forms a colloidal solution in water. Its detergent action is due to its ability to emulsify the greasy matter that holds the dirt particles fast on the soiled linen. With the removal of the grease the dirt is released from the surface of the linen and is washed away.

(vii) *Rubber plating.*—The latex, i.e., the milky juice that a rubber plant yields, is a colloidal suspension of negatively charged rubber particles : this property is taken advantage of to plate rubber by electrophoresis on various objects, e.g., gloves, hot water containers, etc., are made in this way.

Besides, paints, lacquers, varnishes and enamels are dispersions of pigments etc. in suitable vehicles or solvent. Practically all plastics are colloids, so also the gums, resins and glues. Silica and alumina gels find use as adsorbent for gases.

(viii) *Purification of water.*—Alum is largely used for clarifying drinking water. Flocculent precipitate of aluminium hydroxide is formed due to the alkalinity in water—it is in colloid state with a positive charge and readily coagulates the negatively charged colloidal suspensions in the water, and as it slowly settles, it carries with it most of the suspended matter.

Exercises

1. Write a short eassy on the colloidal state of matter. *Punjab*, 1932

2. What are colloids and crystalloids ? Give examples. Discuss some of the important properties of a colloid. Describe a process by which a colloid can be obtained in a pure state.

3. What is dialysis ? Describe an experiment to illustrate it. *Calcutta*, 1958

XV

THE STRUCTURE OF MATTER

In the nineteenth century the atom was regarded as a small indivisible particle —the unit of matter in all chemical changes. But convincing researches in physics of the celebrated scientists, Sir J. J. Thomson, Lord Rutherford and others equally famous in the beginning of the 20th century have shown that an atom is a complex structure.

Cathode rays : The electron.—When an electric discharge is sent through a rarefied gas (at low pressure of 0.1 mm. of Hg or less) in a vacuum tube, a stream of rays, called *cathode rays*, is emitted from the surface of the cathode and move in straight lines towards the anode. By studying the deflection in electric and magnetic fields Sir J. J. Thomson (1897) showed that the cathode rays consist of negatively charged particles. Each particle carries a negative charge of electricity of magnitude 1.6×10^{-19} coulombs which is equal but opposite to that of a hydrogen ion. These negatively charged particles are called *electrons*. The ratio of the charge e to the mass m of the electron, e/m, is 1.758×10^{8} coulombs per gram. The ratio e/m for the electron is always the same, no matter what is the residual gas in a vacuum tube and the material of the cathode. The ratio e/m is 1836 times greater than the ratio of charge to mass, e′/m′, for the hydrogen ion, which is $96{,}494/1.008 = 9.574 \times 10^{4}$ coulombs. Since the charge of an electron is *equal* but opposite to that of the hydrogen ion, i.e., $e = e'$, its mass is 1836 times smaller.

$$\frac{e/m}{e'/m'} = \frac{1.758 \times 10^{8}}{9.574 \times 10^{4}} = 1836, \quad \therefore \quad m' = 1836\ m,$$

i.e., the hydrogen ion is 1836 times heavier than an electron.

Electrons can be had from all kinds of substances. *An electron is*, therefore, *a common constituent of all kinds of matter.* Hence *an electron is a constituent of all atoms.*

The positive rays : The Proton.—The discovery of the electron suggests that an atom contains positive electricity in some form since the atom as a whole is electrically neutral. Besides negatively charged cathode rays, the operation of a discharge tube always produces a stream of rays travelling in a direction opposite to the cathode rays, called *positive rays.* The *positive* rays consist of positively charged particles of atomic mass formed from atoms by the removal of electrons—the ratio of the charge to the mass of these particles is no longer constant as for the electron but depends on the nature of the residual gas in the tube. This ratio shows that these particles are much heavier than the electrons. The lightest positively charged particle has been detected in the hydrogen discharge tube—its mass is about the same as that of the hydrogen atom and it has a unit positive charge, i.e., *it is a hydrogen atom that has lost the electron. This particle of unit mass and unit positive charge* is known as a *proton.* No positively charged ion has been found which has a mass less than that of a proton—the mass of different ions are integral multiples of that of proton. Hence, *protons like the electrons, enter into the structure of all kinds of atoms. A proton is a fundamental particle like an electron.* A proton with one electron forms a hydrogen atom and hence :

$$\text{mass of a H-atom} = \text{mass of a proton} + \text{mass of an electron}$$

$$= 1836\text{ m} + \text{m} = 1837\text{ m},$$

i.e. *the hydrogen atom is* 1837 *times heavier than the electron.*

The Neutron.—*Neutron* is another fundamental particle of matter, discovered by Chadwick in 1932 by bombarding beryllium with alpha particle (i.e., a particle of mass equal to 4 times that of a hydrogen atom and carrying 2 unit positive charges). The neutron has about the same mass as that of the proton, but no electric charge, i.e., it is a neutral particle of unit mass.

Positron was discovered in 1932 by Anderson. A positron is an exact electrical opposite of an electron, i.e., a positron is a positive electron of unit positive charge and mass equal to that of an electron—its place, if any, in the structure of matter is still obscure. A positron has only transitory existence.

The structure of the atom.—The fundamental particles, electrons, proton and neutron, enter into the structure of matter. The present conception about the structure of atom is mainly due to E. Rutherford (1911) and is based on his experiment on the *scattering of α-particles* by thin metal foils. When a thin gold foil, 0.0004 mm. in thickness, for example, is placed in the path of α-particles in a vacuum tube, most of the particles pass out practically without any deflection—a small proportion, however, are scattered through a large angle ; one α-particle in 20,000 was turned through 90° or more. This sudden and very large deflection suggests that the mass of the atom is located on a very minute nucleus, carrying the whole of the positive charge (fig. 51).

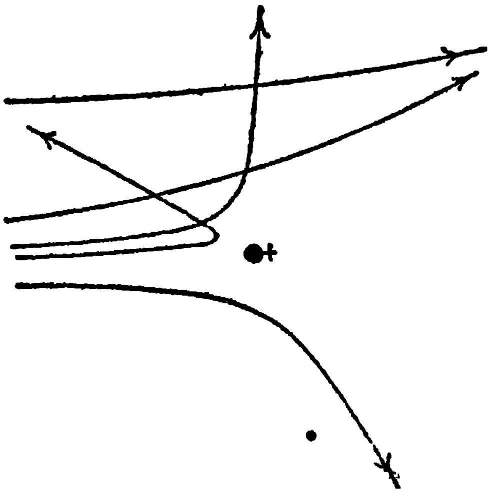


Fig. 51

The size of the nucleus must be very small indeed in comparison with the atom, since the α-particles pass through several atoms without deflection—the diameter of the atom is of the order 10^{-8} cm. and that of the atomic nucleus is of the order of 10^{-12} cm. and hence the greater part of the atom is empty space. The atom is pictured as a system in which a tiny positively charged nucleus is surrounded by *planetary electrons*—an atom is, therefore, very much like a model of the solar system. Since an atom as a whole is electrically neutral, it must contain equal number of protons and planetary electrons. The planetary electrons revolve round the positively charged nucleus in a series of orbits in which they are held, not by gravity as in a solar system, but by electrostatic forces between the positive and negative charges.

Nucleus ←——————Electron——————→

+ Electrostatic attraction — Centrifugal force

The nucleus of an atom is built up of protons and neutrons—the mass of an atom being concentrated entirely in the nucleus. Since the neutrons, like protons, have unit mass but carry no electric charge, the *atomic mass* of an element is equal to the total number of protons and neutrons (the mass of electrons being negligibly small), while the number of protons is equal to the nuclear positive charge.

The proportion of protons and neutrons, however, can vary only within narrow limits, beyond which the nuclei are no longer stable, as in the case of heavy radio-active elements such as radium and uranium.

The atomic number *of an element is equal to the number of positive charges on the nucleus of an atom,* which is equal to the number of protons in the nucleus (also equal to the number of planetary electrons). As the atoms of each successive element in the periodic table has one additional positive charge in the nucleus, the serial number of an element in the periodic table counting from hydrogen is also known as the atomic number. Moseley showed that the atomic number is a more fundamental property of an element than its atomic weight.

The planetary electrons revolve in a set of concentric elliptical shells or orbits having the positive nucleus at the centre. There are seven such shells, each shell being able to contain a certain maximum number of electrons—the first shell which is the nearest orbit to the nucleus can contain only up to 2, the second up to 8, and so on.

The shells are described by the letters K, L, M, N, O, P, etc.,—the first is the K shell, the second L, and so on ; *each shell represents a definite energy level*—the energy is the least when $n = 1$ and increases as the value of n increases, n being the serial number of the shell. The electrons in the K orbit are, therefore, at the lowest energy level.

The maximum number of electrons in a shell n is $2n^2$.

Sheel	n	Maximum number of electrons
K	1	$2\times1^2=2$
L	2	$2\times2^2=8$
M	3	$2\times3^2=18$
N	4	$2\times4^2=32$

The outermost shell of an atom, however, cannot have more than 8 electrons, except helium which has a pair of electrons only.

The electronic configurations of the inert gases with which end the different periods in the periodic table are as follows :

Inert gases and their atomic number		Electrons in successive shells					
		Shell K n = 1	L 2	M 3	N 4	O 5	P 6
Helium	2	2					
Neon	10	2	8				
Argon	18	2	8	8			
Krypton	36	2	8	18	8		
Xenon	54	2	8	18	18	8	
Radon	86	2	8	18	32	18	8

As the charge on the positive nucleus is increased by one at each step an electron is added to the orbits, as the following illustrations clearly show.

An atom of hydrogen contains one proton in the nucleus and a single planetary electron in the first shell ; hence its atomic mass is one, and the atomic number is also one. The helium nucleus contains 2 neutrons and 2 protons—the planetary electrons are therefore two, all contained in the first shell. The next heavier element contains 4 neutrons and 3 protons in the nucleus—the planetary electrons being three only, 2 in the first shell and 1 in the second. The addition of electron in the second shell produces successively the elements lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine and neon—with neon the second shell contains 8 electrons and is full. The next electron successively enters the third shell until it is full in argon—argon having 2 electrons in first shell, 8 in the second and 8 in third.

Atomic structure of first 20 elements in the Periodic Table

Element	Atomic weight	Atomic number	Electrons in orbits			
			K	L	M	N
H	1.008	1	1			
He	4.003	2	2			
Li	6.940	3	2	1		
Be	9.013	4	2	2		
B	10.820	5	2	3		
C	12.010	6	2	4		
N	14.008	7	2	5		
O	16.000	8	2	6		
F	19.000	9	2	7		
Ne	20.183	10	2	8		
Na	22.997	11	2	8	1	
Mg	24.32	12	2	8	2	
Al	26.98	13	2	8	3	
Si	28.09	14	2	8	4	
P	30.975	15	2	8	5	
S	32.066	16	2	8	6	
Cl	35.457	17	2	8	7	
A	39.944	18	2	8	8	
K	39.100	19	2	8	8	1
Ca	40.80	20	2	8	8	2

Electronic Theory of Valency.—Modern atomic structure largely explains the mechanism of chemical changes. The elements of zero group viz., helium, neon, argon, krypton, xenon and radon, are found to be inert chemically, i.e., they manifest no combining capacity, or what is called valency. Their chemical inertness is due to the stable electronic structure of their atoms.

The outermost shell of atoms of all the inert gases, except helium (which has two electrons only), contain eight electrons, as shown in a table on page 155.

Chemical reactivity of other elements depends upon their tendency to assume the stable configuration of the inert gases so as to have an octet in the outermost orbit (or a duplet as in helium). This tendency may be satisfied either (a) by the *transfer* of electrons from one atom to another, or (b) by the *sharing* of electrons between two atoms, accordingly there are two main types of valency, viz., *electrovalency* and *covalency*. The electrons in outermost orbits are usually involved in chemical changes.

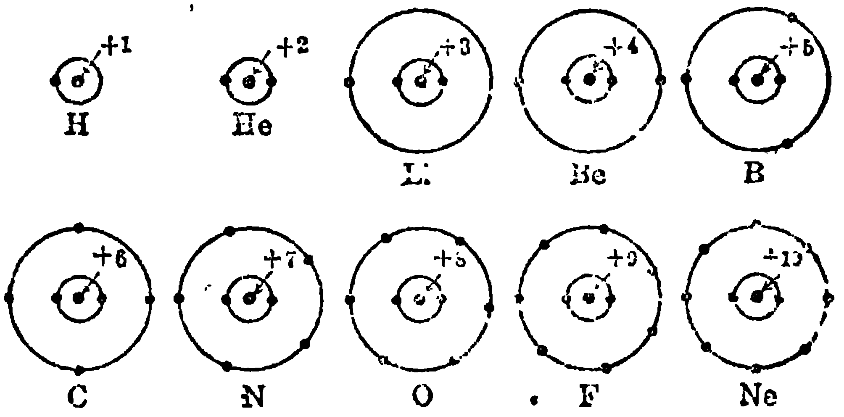


Fig. 52

Electrovalency.—An examination of the atomic number shows that the inert gases are just *followed* by an alkali metal and *preceded* by a halogen. Metals in general follow the inert gases, while the non-metals precede them. The sequence is as follows :

	H	He	Li	
	1	2	2, 1	
O	F	Ne	Na	Mg
2, 6	2, 7	2, 8	2, 8, 1	2, 8, 2
S	Cl	A	K	Ca
2, 8, 6	2, 8, 7	2, 8, 8	2, 8, 8, 1	2, 8, 8, 2

The combination between metals and non-metals, therefore, involves a process of electron transfer in which the surplus electrons of the metal supplies the deficit of electrons of the non-metal. Thus when an atom of sodium with one surplus electron combines with an atom of chlorine with a deficiency of one, producing common salt, sodium transfers the surplus electron to chlorine and thereby satisfies their tendency to lose or gain electrons. The sodium atom has become positively charged owing to the loss of an electron and the chlorine atom negatively charged due to the gain of an electron. The electrically charged atoms, called ions, are then held together by electrostatic attraction, there being no definite bond between them. The ions come apart readily in solution or in the fused state and form independently mobile ions, and hence conduct electric current.

This type of valency which depends upon electron transfer is called *electro-valency*. It may be either *positive* or *negative* and is measured by the number of electrons a neutral atom *loses or gains* in the formation of the complete octet—a metal atom exhibiting positive electrovalency and the non-metals negative electrovalency. In common salt sodium has the positive electrovalency of one, and chlorine the negative electrovalency of one. In the formation of calcium chloride, an atom of calcium transfers its two surplus electrons to two atoms of chlorine—each accepting one electron;

hence calcium develops the positive electro-valency of two. In sodium sulphide two atoms of sodium—each having only one surplus electron—transfer 2 electrons to sulphur atom which has the deficit of two ; sulphur, therefore, has the negative electrovalency of two in this case.

The electron transfer is illustrated by few examples :

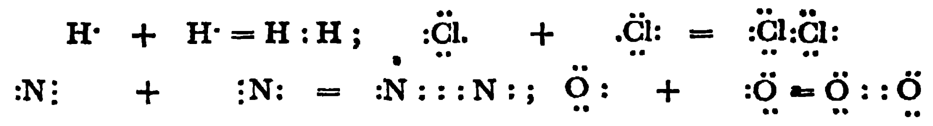
$$\begin{array}{ccccccc} \text{Na} & + & \text{Cl} & = & \text{Na}^+ & + & \text{Cl}^- \\ 2,8,1 & & 2,8,7 & & 2,8 & & 2,8,8 \end{array}$$

$$\begin{array}{ccccccccccc} \text{Cl} & + & \text{Ca} & + & \text{Cl} & = & \text{Cl}^- & + & \text{Ca}^{++} & + & \text{Cl}^- \\ 2,8,7 & & 2,8,8,2 & & 2,8,7 & & 2,8,8 & & 2,8,8 & & 2,8,8 \end{array}$$

$$\begin{array}{ccccccccccc} \text{Na} & + & \text{S} & + & \text{Na} & = & \text{Na}^+ & + & \text{S}^{=} & + & \text{Na}^+ \\ 2,8,1 & & 2,8,6 & & 2,8,1 & & 2,8 & & 2,8,8 & & 2,8 \end{array}$$

Covalency.—The covalency consists in the mutual sharing of a pair of electrons between two atoms each of which has the deficit of electrons—of the shared pair each atom contributes one electron. Mutually shared electrons form a definite bond between the two atoms—the sharing of one, two or three pair giving rise to a single, double or a triple bond respectively. The atoms of non-metals which have the deficit of electrons combine with one another by covalency.

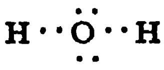
The diatomic molecules, H_2, Cl_2, O_2, N_2, etc., are formed in the following way—the electrons in the outermost orbit being shown only.



$$H\cdot + H\cdot = H:H;\quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: = :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$$

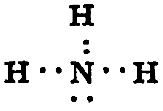
$$:N\vdots + \vdots N: = :N:::N:;\quad \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} = \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}$$

The formation of water, methane, ammonia, ethylene, acetylene and hydrogen chloride by covalent links is shown as follows :



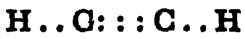
$$H\cdot\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\cdot\cdot H$$

Water



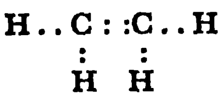
$$H\cdot\cdot\overset{\overset{H}{:}}{\underset{\cdot\cdot}{N}}\cdot\cdot H$$

Ammonia



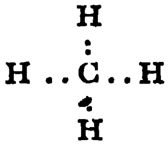
$$H..C:::C..H$$

Acetylene



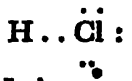
$$H..\underset{\underset{H}{:}}{C}::\underset{\underset{H}{:}}{C}..H$$

Ethylene



$$H..\overset{\overset{H}{:}}{\underset{\underset{H}{:}}{C}}..H$$

Methane



$$H..\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$$

Hydrogen chloride

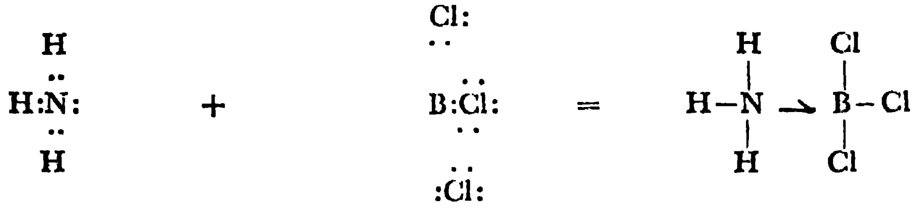
The covalent link due to a shared pair of electrons gives rise to a definite bond between the atoms, while in electrovalent compounds the electrically charged atoms are held together by electrostatic attraction only—there being no bond in between them. This gives rise to difference between electrovalent and covalent compounds :

Electrovalent compounds	**Covalent compounds**
1. Polar and conducts electricity when fused or dissolved.	1. Non-polar and non-conductors.
2. Relatively high melting and boiling points.	2. Relatively low melting and boiling points, i.e., volatile.
3. Usually insoluble in non-ionising solvents, such as benzene.	3. Usually soluble in non-ionising solvents (organic solvents).

Properties of a typical ionic and covalent substance are shown in the table :—

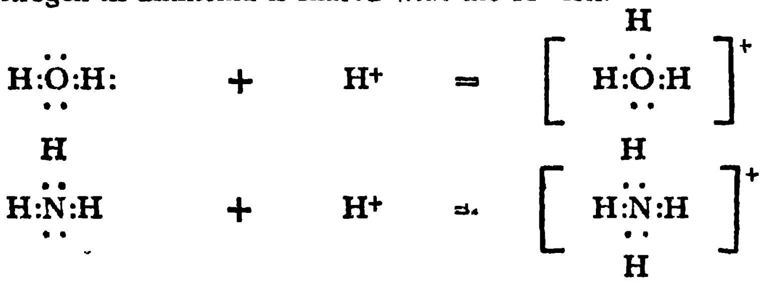
Substance	Type	m.p.	b.p.	Solubility		Conductivity
				in water	in alcohol	in aqueous solution
Common salt	Ionic : highly polar	800°	1440°	high	nil	high
Iodine	Covalent ; non-polar	114°	184°	very slight	high	nil

Co-ordinate covalency—also called dative covalency, *semi-polar bond, co-ionic bond or co-ordinate link.* The co-ordinate link is formed by the sharing of a pair of electrons, but the electrons are contributed by *one atom only,* and not by each atom as in covalency. Here one atom which contains a 'lone pair' of unshared electrons acts as the *donor,* while the other atom acts as the *acceptor.* Thus boron trichloride combines with ammonia—ammonia having a lone of pair of electrons and boron in boron trichloride having only 6 shared electrons in the outermost shell, which is 2 less than the octet. Here ammonia is the donor and boron trichloride the acceptor.



The co-ordinate link is represented by the arrow → with the head pointing towards the acceptor.

In aqueous solutions H^+ ions of acids combine with water by co-ordinate bond, forming *hydronium* ion, H_3O^+—a lone pair of electrons of oxygen in water is shared with the H^+ ion. Ammonium ion, NH_4^+ is similarly formed—the lone pair of electrons of nitrogen in ammonia is shared with the H^+ ion.



Isotopes.—*The atoms of an element with different atomic weights but the same chemical properties are known as isotopes.* Isotopes of an element have the *same atomic number* (i.e., the same number of protons in their nuclei) and hence the same chemical properties. The atomic number determines the planetary electrons in the orbits, and hence also the electrons in the outermost orbit (known as *valency electrons*), upon which depend the chemical properties of an element. The atomic number is, therefore, the fundamental property of an element which determines its chemical property. Isotopes are identical in all properties including the chemical properties, which depend on the atomic number, but differ in those physical properties, such as density, rates of diffusion, etc. which depend on mass. Isotopes (*isos,* equal and *topos,* place) occupy the same place in the periodic table.

It is the number of neutrons in the nucleus which makes the difference in the atomic masses of various isotopes of the same element and not the number of protons which is constant for all the isotopes of a given element—the number of neutrons varies in the different isotopes. Chlorine, for example, has two isotopes of atomic masses 35 and 37—one containing 17 protons and 18 neutrons in the nucleus, while the other contains 17 protons and 20 neutrons only—the atomic number in each case being 17. The atomic mass of an isotope (also known as the *mass number*) which is the sum of the protons and neutrons in the nucleus is always a whole number, since protons and neutrons are particles of unit mass. The atomic weight of an element, as determined by chemical analysis, is but *an average of the atomic masses of various isotopes of an element as found in nature.*

Elements with fractional atomic weights exist as mixture of isotopes whose mass numbers have integral values.

Thus ordinary chlorine contains the two isotopes of atomic masses 35 and 37 in such a proportion that its average atomic mass is always found to be 35.457. Argon has three isotopes of atomic mass 40, 38 and 36 and its average atomic mass is 39.944. Potassium has three isotopes of atomic mass 39, 40 and 41, and its average atomic mass is 39.10. The atomic numbers of argon and potassium are 18 and 19 respectively, and hence quite correctly argon precedes potassium in the periodic table.

Hydrogen has three isotopes—'light hydrogen', heavy hydrogen or deuterium (symbol D) and tritium of mass numbers 1, 2 and 3 respectively. Relative abundance of deuterium in ordinary hydrogen is about 1 part of deuterium to 6900 of 'light hydrogen' and ordinary water contains corresponding amount of heavy water, D_2O.

The principal method of enrichment of ordinary water in *heavy water*, also called *deuterium oxide*, D_2O, is electrolysis of aqueous solution of acid or alkali ; light hydrogen is preferentially evolved, and the residual solution gets richer in deuterium with progress of electrolysis. Heavy water can be finally obtained by prolonged electrolysis Deuterium is made by the action of sodium on deuterium oxide or by electrolysis of deuterium oxide in presence of phosphorus pentoxide.

Oxygen has 3 isotopes of mass numbers 16, 17 and 18. Uranium has three isotopes of mass 234, 235 and 238—the 235 isotope readily undergoes *nuclear fission* with explosive violence releasing huge energy as it does in the *atom bomb*. **Isotopes of few elements are :**

Elements	Atomic number	Atomic weight	Mass number	proton+neutron Nucleus
Hydrogen	1	1.008	1	1
			2	1+1
			3	1+2
Chlorine	17	35.457	35	17+18
			37	17+20
			36	18+18
Argon	18	39.944	38	18+20
			40	18+22
			39	19+20
Potassium	19	39.100	40	19+21
			41	19+22

Isotopes of different elements having the *same mass* numbers are known as **isobars** : this occurs when the sum of protons and neutrons in their nuclei is the same. The two isotopes of argon and potassium with mass numbers 40 are isobaric. Except that they have the same atomic mass, the isobars differ in all their physical as well as chemical properties.

Atomic structure and atomic theory.—Modern atomic structure contradicts the assumptions of Dalton's atomic theory.—(i) An atom is not indivisible, as Dalton assumed, since it itself consists of the fundamental particles, protons, neutrons and electrons. (ii) The discovery of isotopes indicates that the atomic weight of an element is not constant as was the assumption of Dalton. In the light of modern theory of the atom *an element may be defined as a substance which is composed of atoms with same atomic number i.e., with the same positive charge in the nucleus.*

But the most fundamental assumption of the atomic theory—that an atom is the unit of all chemical changes still holds good, in spite of its complex structure.

RADIOACTIVITY

Discovery.—The walls of X-ray generating vacuum tube become luminous or *fluoresce* under the influence of X-rays. Fluorescent substances were, therefore, carefully examined for a supposed relation between fluorescence and X-rays. It was in this context that is 1896, one year after the discovery of X-rays by Rontgen, uranium compounds were found by H. Becquerel to spontaneously emit radiations capable of affecting a photographic plate covered in black paper. This spontaneous emission of penetrating rays was called *radioactivity* and the element uranium undergoing such a change is said to be *radioactive*. In course of investigation of the uranium mineral, *pitchblende*, which was found to be more active than its uranium content, M. and Mme. Curie in 1899 discovered two active elements, *polonium* (so named after Mme. Curie's native country, Poland) and *radium*, which were many times more active than uranium itself. Another radioactive element, *thorium*, occurs in *monazite sands*, found in Travancore in India.

Fig. 53
Madame Curie (1867-1934)

Properties.—The radiation emitted by radioactive elements is composite in nature and consists of three different kinds of rays : *the α-rays*, *the β-rays* and *the γ-rays*. When subjected to an electric or magnetic field (fig. 54) the α-rays suffer deflection in the opposite direction to β-rays, whereas the γ-rays remain undeflected.

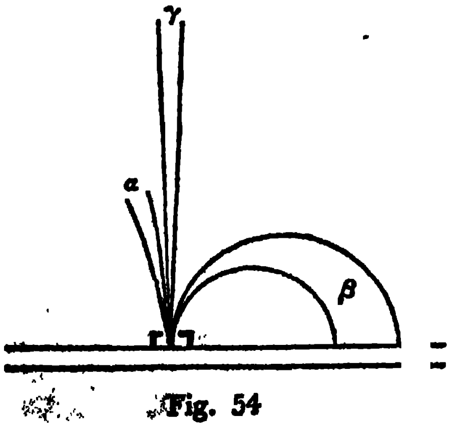


Fig. 54

The α-rays consist of material particles of mass 4 and having a positive charge of 2 units, i.e., they are *doubly positively-charged helium atoms*. They are shot out with a velocity about one-tenth that of light.

They have great ionising power but very little penetrating power—only a few cm. of air or very thin aluminium foil, 0.01 mm. in thickness. When radium (atomic mass 226) emits α-particles, the inert gas radon (atomic mass 222) is formed, the atomic mass of an α-particle being 4. One element is thus transformed into another element with emission of rays in a radioactive change. The α-particles ultimately become helium.

The *β-particles* consist of electrons, i.e., particles of unit negative charge, shot out with speeds varying from two-fifths to nine-tenths of speed of light. Particles with high speed have considerable penetrating power—0.1 mm. of aluminium. Their ionising power is much weaker than α-rays. The γ-rays are not particulate but are X-rays, i.e., electro-magnetic radiations, of very short wave length. They are not deflected by either electric or magnetic fields. The speed of γ-rays is the same as that of light, 186,000 miles per second. They ionise air and are highly penetrating—25 cm. of steel and 5 cm. of lead.

The penetrating power of the rays is roughly in the order 1,100 and 10,000 for the α-, β-, and γ-rays.

Radioactivity is an atomic phenomenon, i.e., it is the characteristic of the atom of the element undergoing the change, irrespective of its state of combination or past history. Radioactive change is unaffected by temperature, pressure, etc. New elements are produced in a radioactive change.

When nitrogen gas is bombarded with swift α-particles, the former is transformed into oxygen with release of protons :

$${}_7N^{14} + {}_2He^4 \text{ (alpha-particle)} = {}_8O^{17} + {}_1H^1 \text{ (proton).}$$

where the subscripts are atomic numbers and the superscripts are the atomic masses.

This is an example of **artificial transmutation of elements,** first brought about by E. Rutherford in 1919. This experiment *inter alia* also proves that the *nuclei of atoms contain protons.*

Artificial radioactivity was discovered by Irene Curie, the daughter of the discoverers of radium, and her husband F. Joliot in 1932, while studying the effect of fast α-particles on boron, aluminium and magnesium—they noted that positrons were emitted, in addition to neutrons. The bombarded elements were transformed into new elements with emission of neutrons. The new elements so produced disintegrated like radio-active elements, although positrons were emitted instead of α- or β-particles.

Magnesium, for example, was transformed into radio-silicon, which in its turn disintegrated into a stable isotope of aluminium with emission of positrons :

$${}_{12}Mg^{24} + {}_2He^4 = {}_{14}Si^{27} + {}_0n^1 \text{ (neutron)}$$

$${}_{14}Si^{27} = {}_{13}Al^{27} + \beta^+ \text{ (positron)}$$

This result is a conclusive evidence of *artificial transmutation of atoms* first noted by E. Rutherford in 1919.

Most artificial radioelements decay with emission of electrons or positrons.

Exercises

1. Make a short note on the structure of atom.

2. Explain the terms : electron, neutron, atomic number and co-valency. The nucleus of an atom of an element consists of 12 neutrons and 11 protons. What is the atomic weight and electrovalency of the element ? Give the electronic structure of : (i) helium atom, (ii) carbon atom.

3. Explain clearly the terms : electrovalency, covalency and co-ordinate covalency. How would you explain, on the basis of electronic theory of valency the formation of the following molecules : (i) LiF, (ii) F_2, (iii) O_2, and (iv) CH_4 ?

XVI

THE PERIODIC CLASSIFICATION OF ELEMENTS

Evolution of Periodic Law.—There have been many attempts to classify elements according to their similarities—they have been broadly classified, for example, into metals and non-metals, but their distinction is not always very sharp. The most satisfactory system of classification of elements is based on their atomic weights.

Fig. 55
Mendeleeff (1834-1907)

As early as 1817, Dobereiner noticed that the atomic weights of chemically related elements vary in a regular manner,—viz., in a set of three such elements the atomic weight of the middle elements is approximately the arithmetic mean of those of the extreme elements ; thus, taking the modern atomic weights, we have :

Cl	35.5	Ca	40	S	32
Br	80	Sr	88	Se	79
I	127	Ba	137	Te	128

This is known as the **law of triads.**

In 1862 de Chancourtois arranged the elements in the order of their increasing atomic weights in a spiral around a cylinder divided into several vertical strips and noticed that similar elements fell on the same vertical of *de Chancourtois helix*.

But serious attempts were made to discover relations between the properties of various elements and their atomic weights only after a sound system of atomic weights had been worked out by Cannizzaro in 1857.

In the year 1864 Newlands actually attempted a classification of elements on the basis of their atomic weights and stated that *if the elements are arranged in the order of their increasing atomic weights, the eighth element from a given one is a kind of repetition of the first, like the eighth note in an octave of music.* This is referred to as the **law of octaves.** His observation was but very coolly received.

But nevertheless, the ideas of de Chancourtois and Newlands contained the germ of the Periodic Law.

The Periodic law.—From the consideration of chemical properties, the great Russian chemist Dimitri Mendeleeff enunciated the principle of periodic classification of elements in the year 1869.

Mendeleeff observed that "there must be some bond of union between mass and chemical elements ; and as the mass of a substance is ultimately expressed in the atom, a functional dependence should exist and be discoverable between individual properties of elements and their atomic weights" and he found that "*if the elements are arranged in the order of their increasing atomic weights, their properties vary in a regular manner from a member to member of the series, but return more or less to the same value at certain fixed points in the series*" *i.e., the elements show periodicity in properties or in short :*

The physical and chemical properties of elements are periodic functions of their atomic weights. This is known as the **periodic law** *of elements.*

Similar generalisation was arrived at independently by the German chemist Lothar Meyer in the same year from his observations on the physical properties of elements.

The Periodic table.—On the basis of the periodic law Mendeleeff arranged the elements in a table (called the periodic table) which is a list of the elements in the order of ascending atomic weight—the table was prepared by cutting the list of the elements into successive horizontal rows (called *periods*) in such a way that similar elements come under the same vertical columns (called *groups*). A modern version of Mendeleef's periodic table consists of 9 groups, number I to VIII and 0 (zero), and seven periods containing 102 elements.

Except the first period which begins with hydrogen, each period begins with an alkali metal, and ends with an inert gas. Passing though the table we have in succession :

Period	Number of elements	Elements
1	2	H and He
2 (first short period)	8	Li to Ne
3 (second short period)	8	Na to A
4 (first long period	18	K to Kr
5 (second long period)	18	Rb to Xe
6 (first very long period)	32	Cs to Rn
7 (second very long period)	16	Fr to No

The first period contains 2 elements ; each of the second and third periods contains 8 elements. The properties of elements of the second period are more or less reproduced in the elements of the third period :

Period 2	Li	Be	B	C	N	O	F	Ne
Period 3	Na	Mg	Al	Si	P	S	Cl	A

Thus, lithium and sodium are alkali metals which decompose cold water ; fluorine and chlorine are halogens which readily unite with metals to yield salts, and so on.

Every ninth element, therefore, starting from a given element, is a kind of repetition of the first. *The elements of the first and second short periods* are referred to as **typical elements.**

The fourth and fifth periods of 18 elements each are divided into *even* and *odd* series according as the elements occur in series of even (e.g. K) or odd (e.g. Cu) number, starting with hydrogen.

After argon 18 elements are passed over before the next inert gas krypton is reached—the periodic recurrence of properties begin only after 18 elements, e.g., potassium is analogous to rubidium ; bromine is analogous to iodine. This is due to the *inter-position* of 10 elements, called the **transition elements,** scandium (21) to zinc (30), which bear little or no analogy with the typical elements. The remaining 8 elements, e.g., K, Ca, and Ga to Kr bear a close analogy to the typical elements of short periods.

The first long period is followed after krypton by a second long period where an identical sequence is met with—the 10 elements yttrium (39) to cadmium (48) form the second series of transition elements. The remaining 8 elements, e.g., Rb, Sr, and In to Xe are analogous to the members of the short periods.

The 6th (first very long period) period contains 32 elements : Cs, Ba, the elements of the rare earths, etc., and Rn. As in the long periods, there are 8 elements : Cs, Ba, and Tl to Rn which are closely related to the typical elements. Of the remaining 24 elements, 14 elements **cerium (58) to lutecium (71)**— are so remarkably similar to one another that they are placed in the same position in the periodic table ; they are known as **rare earth elements,** also called **lanthanides.** The remaining 10 elements, e.g., lanthanum (57), and hafnium (72) to mercury (80) form the third series of transition elements.

An identical sequence of the 6th period recurs in the incomplete second very long period in which the **actinide series** begins after actinium and abruptly ends with nobelium. The elements neptunium to nobelium are known as **transuranic elements,** as they are placed beyond uranium in the periotic table.

The position of *transition elements, lanthanides* and *actinides*, is clearly shown in the Long Periodic Table.

Groups and sub-groups of elements.— Due to the interposition of the transition elements, the members of the long periods have been divided into the sub-groups *a* and *b*—elements occuring in the first part of a long period are called sub-group *a*, those in the second part sub-group *b*. The typical elements resemble the sub-group which does not contain the transition elements—the transition elements constituting the *b* sub-group in groups I and II, and the *a* sub-group in groups, III, IV, V, VI and VII. Each of the groups I to VII consists of two typical elements and two sub-groups of the long periods. Near the end of the table in group I the typical elements and the sub-group Ia are closely related and are called the **alkali metals**—the **coinage metals** of sub-group Ib do not resemble the alkali metals ; while in group VII the typical elements and the sub-group VIIb form the family of halogens—manganese of sub-group VIIa being quite different from the halogens. In the middle of the table, especially in group IV, the two sub-groups are about equally related to the typical elements. The inert gases occupy the zero group in the table, while the group VIII is a compact body of nine metals of the transition series.

Periodicity in properties.—There is a regular gradation of properties of elements in the same period, as also in the same group—the properties of an element are, as a rule, intermediate between those of the contiguous elements in the table and are, therefore, dependent upon its position in the table, and hence upon its atomic weight, i.e.; *the magnitude of the atomic weight determines the character of an element.*

Periodicity of physical properties.—The physical properties of elements show the same periodicity as their chemical properties.

The Long periodic table · The Bohr Table

Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	IIIb	IVb	Vb	VIb	VIIb	0
H 1																	He 2
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12	←——— Transition elements ———→										Al 13	Si 14	P 15	S 16	Cl 17	A 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La* 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac** 89															

*Lanthanides	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
**Actinides	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	E 99	Fm 100	Mv 101	No 102	

Elements 93 to 102, viz., neptunium, plutonium, americium, curium, berkelium, californium, einsteinium, fermium, mendelevium and nobelium are known as *transuranic elements*.

Modern version of Mendeleef's Periodic Table

Periods	Series	Group																	
		I		II		III		IV		V		VI		VII		VIII			0
		a	b	a	b	a	b	a	b	a	b	a	b	a	b				
1	1	H 1 1.008																	He 2 4.003
2	2	Li 3 6.940		Be 4 9.013			B 5 10.82		C 6 12.01		N 7 14.008		O 8 16.00		F 9 19.00				Ne 10 20.183
3	3	Na 11 22.997		Mg 12 24.32			Al 13 26.98		Si 14 28.09		P 15 30.975		S 16 32.066		Cl 17 35.457				A 18 39.944
4	4	K 19 39.10		Ca 20 40.08		Sc 21 44.96		Ti 22 47.90		V 23 50.95		Cr 24 52.01		Mn 25 54.93		Fe 26 55.85	Co 27 58.94	Ni 28 58.69	
	5		Cu 29 63.54		Zn 30 65.38		Ga 31 69.72		Ge 32 72.60		As 33 74.91		Se 34 78.96		Br 35 79.916				Kr 36 83.8
5	6	Rb 37 85.48		Sr 38 87.63		Y 39 88.92		Zr 40 91.22		Nb 41 92.91		Mo 42 95.95		Tc 43 99.0		Ru 44 101.7	Rh 45 102.91	Pd 46 106.7	
	7		Ag 47 107.88		Cd 48 112.41		In 49 114.76		Sn 50 118.70		Sb 51 121.76		Te 52 127.61		I 53 126.91				Xe 54 131.3
6	8	Cs 55 132.91		Ba 56 137.36		La 57* 138.92		Hf 72 178.6		Ta 73 180.88		W 74 183.92		Re 75 186.31		Os 76 190.2	Ir 77 193.1	Pt 78 195.2	
	9		Au 79 197.2		Hg 80 200.61		Tl 81 204.39		Pb 82 207.21		Bi 83 209.00		Po 84 210		At 85 210				Rn 86 222
7	10	Fr 87 223		Ra 88 226.05		Ac 89** 227		Th 90 232.12		Pa 91 231		U 92 238.07							

*Rare Earths (58—71) (*Lanthanides*)	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
**Actinides	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	E 99	Fm 100	Mv 101	No 102	—

This can be shown graphically by a plot of physical properties against atomic weights, as illustrated in the atomic volume curve.

Atomic volume.—Atomic volume is the volume in c.c. occupied by 1 gram atom of the element and is obtained by dividing the atomic weight of the element by its density.

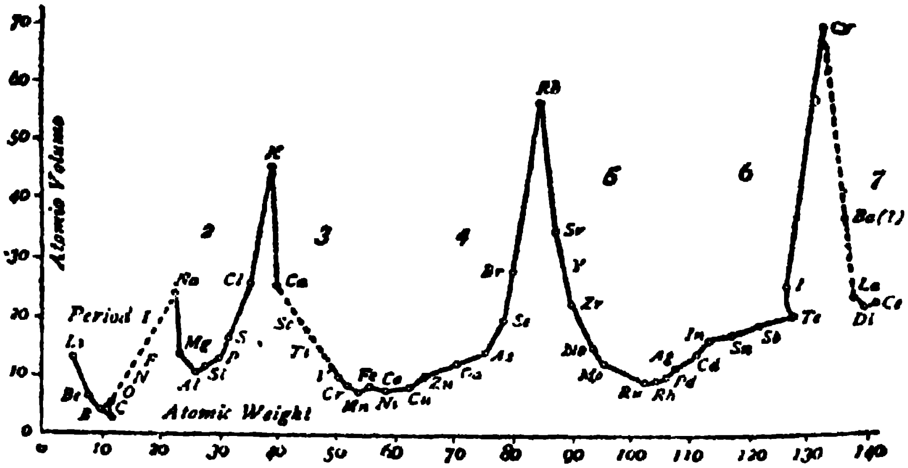


Fig. 56

Atomic volume = atomic weight ÷ density.

Lothar Meyer observed that the atomic volumes of elements showed periodicity when plotted against atomic weights—the members of each period appearing in *successive* positions, while the elements of each group occupying *similar* positions in the atomic volume curve. The curve (fig. 56) shows a series of waves in which the short and long periods are clearly shown, with the light alkali metals at the crests and the heavy transition elements in the troughs of the waves.

The electronegative elements, i.e., mainly non-metals, occur on the ascending part of the curve ; the electropositive elements on the descending parts.

Mendeleeff observed that the reactive elements such as alkali metals and halogens have high atomic volumes, whereas elements which have low atomic volumes, Co, Ni, Ir, Pt, etc., are not very reactive.

The atomic volume curve shows also periodicity in many other physical properties of elements, such as coefficient of expansion, melting and boiling points, hardness and malleability, conductivity for heat and electricity, and so on.

Periodicity of Valency.—The periodic table is above all a valency classification, and as Mendeleeff pointed out the group number of an element is identified with its highest oxygen-valency (i.e., *the highest valency exhibited in its typical oxide*)—in group VIII the highest valency is met with only in OsO_4 and RuO_4. The oxygen valency gradually increases in steps from the left, and the hydrogen valency in steps from the right, as the following illustration indicates :

Group	I	II	III	IV	V	VI	VII
Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Hydride	..	...	...	SiH_4	PH_3	H_2S	HCl

The metals on the left exhibit no hydrogen valency, but in all cases when both the valencies appear, their sum is always equal to eight.

Electro-chemical character.—Periodic relationship.—Each period begins with an alkali metal which is the most electro-positive of the elements in group I and ends with a halogen which is the most electro-negative in group VII. In passing along a period from group I to group VII the elements display a gradual decrease of electro-positive (metallic) character followed by an increase of electro-negative (non-metallic) character—coming at group IV the members show very feeble electro-chemical character, but at group V the electro-positive character changes completely into electro-negative which gradually increases until it becomes a maximum in group VII. This is clearly exhibited by oxides of the third period :

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
strongly basic	basic	amphoteric	weakly acidic	acidic	strongly acidic	very strongly acidic

Acidity of oxides increases from left to right ; in groups I and II oxides are strongly basic, in group III the oxide shows both properties ; whilst in groups IV, V, VI and VII the oxides show increasing acidity. In other words, *electropositive elements give basic oxides* and *electro-negative elements acidic oxides.*

Group relationship.—The electro-positiveness, i.e., metallic character of elements gradually increases with increasing atomic weights in each group. In the fifth group, for example, metallic properties are progressively developed· nitrogen and phosphorus are typical non-metals, arsenic a non-metal with some metallic properties, antimony a metal with some non-metallic character and bismuth a typical metal ; the gradation is also exhibited in their oxides—N_2O_3 and P_2O_3 are distinctly acidic, As_2O_3 mainly acidic with a feeble basic character. Sb_2O_3 amphoteric, Bi_2O_3 predominatly basic.

Diagonal relationship.—The first member of a group resembles the second member of the next group. This is referred to as diagonal relationship. Thus, there are similarities between lithium and magnesium, beryllium and aluminium, and boron and silicon.

Lastly, it must be remembered that the vertical relationship of the typical elements is replaced by *horizontal relationships* in the transition series. Thus, the metals Cr, Mn, Fe, Co, Ni, which are members of the first transition series, bear a close analogy to one another ; all are high-melting solids with high density and low atomic volume ; all of them exhibit variable valency and give coloured ions.

✓ **Uses of the periodic table.**—(i) **The systematic classification of chemically related elements in the same group,**—members the same group having similar properties and giving rise to compounds of analogous structures and properties ; e.g., alkali metals, halogens, alkaline earth metals, and so on.

(ii) **Correction of doubtful atomic weights.**—Since the magnitude of the atomic weight of an element fixes its position in the periodic table, Mendeleeff was able to correct several doubtful atomic weights with the aid of a knowledge of those of adjacent elements. From its occurrence with zinc in minerals, indium was taken to be bivalent, and hence its atomic weight = 38 × 2 = 76, the equivaelnt of indium being 38. But there was no vacant space in the table in group II for an element with the atomic weight 76. Mendeleeff asserted that indium is tervalent and its atomic weight = 38 × 3 = 114 —the element then filling a vacant space in the table in group III between cadmium and tin.

Beryllium was regarded as tervalent owing to its striking similarities with aluminium; but it could only be placed in group II. The atomic weight was, therefore, corrected from 4.5 × 3 = 13.5 to 4.5 × 2 = 9, 4.5 being the equivalent of beryllium.

Subsequent work has generally confirmed the changes so boldly advocated by the Russian chemist.

(iii) **Prediction of missing elements.**—In order that chemical analogies might be preserved Mendeleff in framing the table left many blank spaces for the missing elements and predicted the discovery of yet unknown elements to fill up these gaps. He even ventured to predict their atomic weights and properties from those of the contiguous elements in the table. His anticipations were fulfilled with remarkable accuracy in his life time by the discovery of the elements *scandium*, *gallium* and *germanium* which he called *eka-boron*, *eka-aluminum* and *eka-silicon* respectively (Sanskrit *eka* = one).

The predicted and observed properties of germanium are as follows :

Properties	Eka-silicon predicted in 1871	Germanium discovered in 1886
(i) Atomic weight	72	72.6
(ii) Density	5.5	5.47
(iii) Atomic volume	13	13.2
(iv) Colour	Dirty grey	Greyish-white
(v) Ignition produces	EsO_2, white powder	GeO_2, white powder
(vi) Action on water	Will decompose steam with difficulty	Does not decompose water
(vii) Effect of acids	Slight	HCl has no effect ; soluble in aqua regia
(viii) Effect of alkali	More pronounced than in acids	Aqueous KOH has no action : burns brillianly in molten KOH
(ix) Element produced by	Reduction of EsO_2 or K_2EsF_6 by Na	Reduction of GeO_2 by C or K_2GeF_6 by Na
(x) Properties of oxides	Refractory, density 4.7 ; less basic than TiO_2 or SnO_2, but more basic than SiO_2	Refractory ; density 4.703 ; feebly basic : forms germanates
(xi) Properties of chloride	Liquid, boiling below 100°, density 1.9 at 0°	Liquid, boiing at 86.5° ; density 1.887 at 18°
(xii) Properties of fluoride	EsF_4 will not be a liquid	$GeF_4.3H_2O$ is a white crystalline solid.

The resemblance is highly convincing to show the usefulness of periodic table.

The gaps corresponding with the elements *technetium* 43, *promethium* 61, *rhenium* 75, *polonium* 84, *astatine* 85, and *francium* 87 have been filled up, partly with information supplied by the periodic table.

The discovery of the inert gases were not, however, predicted by the table, and as a matter of fact, Mendeleeff's table had no provision for the zero group elements. When the inert gases were discovered towards the end of the 19h century, they placed in an additional zero group where they bridge the gap between the most o-positive alkali metals of group I and the most electro-negative halogens of p VII.

(iv) The periodic table is of great service in the understanding of structure of the atom.

Difficulties in the periodic table.—The table was not free n its defects and apparent contradictions.

(i) The *inverted positions* of 4 pairs of **misfit elements,** namely, *m* (39.944) and *potassium* (39.100), *cobalt* (58.94) and *nickel* (58.69), *rium* (127.61) and *iodine* (126.91), *thorium* (232.12) and *protonium* (231), where the *heavier* elements have been placed before *lighter* elements on grounds of chemical analogies.

(ii) The *transitional elements* occupy an anomalous position ; due their interposition elements with little analogy have often been iced together, e.g., the alkali metals which show no similarity with e coinage metals have been put together in group I ; managanese is t with the halogens in group VII, though they have but very little al analogy. Sometimes *chemical analogy* has been overlooked ; us copper and mercury, though similar in many properties, have en placed in different groups ; so also is the case with boron and icon.

(iii) Suitable positions for *hydrogen* and the *rare earths* and the tinides are wanting in the table. Mendeleeff's table also fails fix up the exact number of elements in the rare earth series.

Classification based on atomic numbers.—The periodic assification of elements based on atomic weights gives rise to the bove defects, since the atomic weight is not a constant property f an element—the discovery of *isotopes* (i.e., atoms of the same element aving *different* atomic weights but the *same chemical* properties) efinitely establishing that there may be different atomic weights of he same element.

The anomalies of the periodic classification find satisfactory xplanations if the elements are classified in the order of their atomic iumbers—the atomic number is numerically equal to the number of init positive charge in the nucleus of the atom of an element. The periodic law may, therefore, be restated as

"the properties of elements are periodic functions of their atomic numbers."

The modern classification based on atomic number has the following advantages :

(i) Each element occupies a place in the table in a series of integers from one to one hundred and two—the atomic number of the lightest element hydrogen is one and that of nobelium 102.

The possibility of discovery of new elements is, however, by no means exhausted, since the second very long period is incomplete.

(ii) It gives the underlying reason for the correct position of argon, cobalt, tellurium and thorium—their atomic number being one less than those of potassium, nickel, iodine and protoactinium respectively.

(iii) It fixes the exact number of rare earth metals to be 14, from cerium (58) to lutecium (71), both inclusive.

Position of hydrogen in the table.—The lightest element hydrogen (at. wt. = 1.008) has the atomic number one, and hence it must precede helium (atomic number 2) in the periodic table, as shown in the first period: Now, since it resembles both the alkali metals of group I and the halogens of group VII it may be placed in either groups.

Properties of hydrogen compared with alkali metals and halogens :

Alkali metals	*Hydrogen*	*Halogens*
(i) Solid, vapour usually monatomic	Diatomic gas	Gas, liquid or volatile solid ; vapour diatomic
(ii) Metal	Non-metal	Non-metal
(iii) Forms alloys with metals.	Forms *salt-like* hydrides, e.g., LiH and CaH_2	Forms salts with metals
(iv) Forms stable oxides ; e.g., Na_2O.	Forms stable oxides, e.g., H_2O	Forms unstable oxides, e.g., Cl_2O
(v) Reducing agent	Reducing agent	Oxidising agent
(vi) Strongly electropositive, forming stable cations, Na^+, K^+, etc.	Feebly electropositive ; H^+ only found *in vacuo*. Feebly electronegative ; H^- found in $Li^+ H^-$	Strongly electronegative, forming stable, anions, F^-, Cl^-, etc.

Besides,

(vii) Hydrogen forms hydrocarbons in which halogens can replace hydrogen, atom for atom, without any change of type, e.g., CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4.

(viii) Fused lithium hydride, LiH, on electrolysis liberates hydrogen at anode, showing that it may be *electronegative* like halogens.

(ix) Electrolysis of acidulated water liberates hydrogen at cathode—hydrogen is, therefore *electropositive* like alkali-metals.

Considering the points i, ii, iii, and vii and viii hydrogen as a univalent element can be placed in group VII with halogens, but the first period might then contain unknown elements of atomic weights less than 1. Points iv, v and ix and the fact that hydrogen forms an alloy with palladium suggest that hydrogen can be placed in group I with alkali metals ; there would then be 6 gaps in the first period with atomic weights between 1 and 4. It is, however, placed at the head of group I, because it is generally electropositive.

Though a reducing agent and generally electropositive, it is never a metal like alkali metals ; and though a non-metal and sometimes electronegative, it is never an oxidising agent like halogens. Its structure explains its dual character—the hydrogen atom consists of 1 proton and a single planetary electron. Like the alkali metal it may lose an electron and become a positive ion :

$H = H^+ + e$ compare $Na = Na^+ + e$

It may gain an electron to assume the electronic configuration of helium, and may form a negative ion, like the halogens :

$H + e = H^-$ compare $Cl + e = Cl^-$

$Li + H = Li^+H^-$ compare $Li + Cl = Li^+Cl^-$

Hydrogen is thus an unique element—it has no analogues.

Exercises

1. Give a brief account of the periodic classification of elements. Discuss its merits and demerits. Show that the chemical properties of magnesium and zinc justify their position in the same group in the periodic table. *Calcutta*, 1958

2. Write a short account of the periodic classification of elements. Mention the advantages and anomalies of this classification. *U. P. Board* 1943

3. What is meant by Periodic law ? Briefly discuss the main features of periodic classification of elements and discuss the influence of the concept of atomic number upon it.

XVII

OXYGEN, HYDROGEN AND WATER

Oxygen

Symbol O. Formula O_2. Atomic number 8. Atomic weight 16 by definition. M. Pt.—218°C. B. Pt.—183°C. Density, 1 litre at N.T.P. weighs 1.429 grams. Solubility, 1 litre of water at 0°C dissolves 48.9 c.c. of oxygen at 1 atmosphere.

History.—Oxygen was independently discovered by Scheele and Pristley in the year 1774. Scheele obtained the gas by heating various substances, namely, a mixture of nitre and oil of vitriol, red oxide of mercury, etc. ; while Pristley prepared it by heating the latter substance by focussing sun's rays thereon by means of a convex lens. But its importance in combustion and respiration was first clearly recognised by Lavoisier who also gave it the name oxygen.

Occurrence. Oxygen is by far the most abundant of the elements. It occurs *free* in the atmosphere of which it forms about 21% by volume or 23% by weight. In the *combined state* it occurs in *water*, in nearly all *rocks*, in *plants* and in *animals*. It forms about 88.8% of water by weight or 36% *of the ocean*, and nearly 50% of the earth's crust.

Laboratory preparation.—In the laboratory oxygen is usually prepared by heating a mixture of 5 parts of potassium chlorate, $KClO_3$, with 1 part of manganese dioxide, MnO_2. The mixture is taken in a hard glass test tube fitted with a cork through which passes a delivery tube the further end of which dips under water in a pneumatic trough. The test tube is clamped in a horizontal position with its cork-end inclined slightly downwards, fig. 56a.

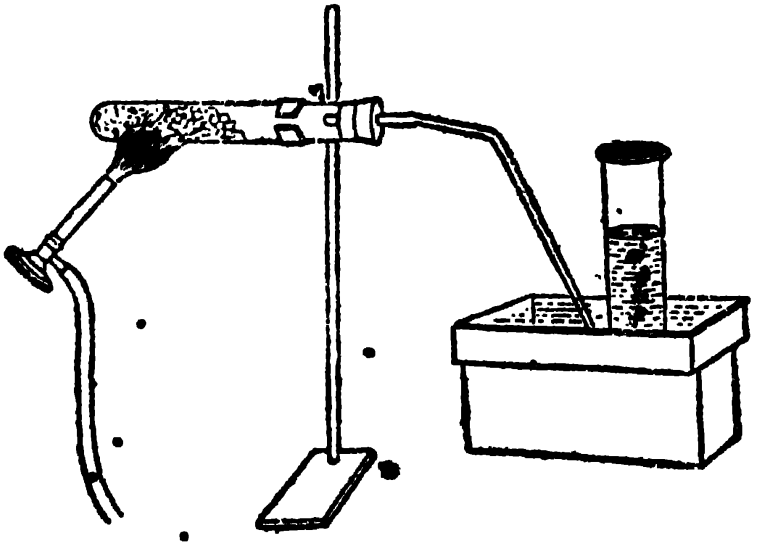


Fig. 56a

The potassium chlorate alone decomposes on heating into potassium chloride and oxygen ; the manganese dioxide acts as .. *catalyst* (p. 145). The liberated oxygen gas is collected *by the displacement of water* as follows : A gas jar completely filled with water and closed with a greased cover glass, is inverted over water, in the trough ; while under water, the cover glass, is removed and the gas jar is placed on the shelf of the trough so that the delivery tube reaches the mouth of the jar through an opening in the shelf. Oxygen collects in the jar by the displacement of water. When the jar is full of the gas, its mouth is closed with a cover glass, while still under water, and it is then removed from the trough. Several jars of oxygen are similarly collected.

$$2KClO_3 \text{ (potassium chlorate)} = 2KCl \text{ (potassium chloride)} + 3O_2.$$

Manganese dioxide adulterated with powdered coal or antimony sulphide explodes violently when heated with potassium chlorate. Hence a *little* of the mixture should be always heated before starting the experiment to make sure that no deflagration occurs.

When heated alone, potassium chlorate melts and rapidly gives off oxygen at 370° to 380°C—two reactions however taking place : $2KClO_3 = 2KCl + 3O_2$.

$$4KClO_3 = 3KClO_4 \text{ (potassium perchlorate)} + KCl.$$

Above 400°C the perchlorate also decomposes, liberating oxygen.

$$KClO_4 = KCl + 2O_2.$$

In presence of a little manganese dioxide potassium chlorate decomposes at less than 240°C. The manganese dioxide can be recovered unchanged in mass and composition at the end of the reaction, and hence acts merely as a catalyst, i.e., it has simply helped the decomposition of potassium chlorate, but it has not undergone any permanent chemical change.

Manganese dioxide simply accelerates the decomposition of potassium chlorate.

This can be illustrated in a simple way. Two hard glass test tubes, one containing potassium chlorate alone, and another a mixture of manganese dioxide and potassium chlorate in the proportion of about 1 : 4, are embedded in sand in a sand-tray and heated. It will be seen that oxygen is evolved first from the tube containing the mixture.

Manganese dioxide remains unaltered in weight and properties when it acts as a catalyst in the decomposition of potassium chlorate.

About 1 gm. of manganese dioxide is put in a tared porcelain crucible containing about 4 gm. of potassium chlorate, and weighed again—the difference gives the weight of manganese dioxide. The crucible is then carefully heated over a small flame on clay-pipe triangle until oxygen ceases to be evolved.

The crucible is then cooled, and put in a beaker of water, and boiled in order to separate from the crucible the residue of manganese dioxide and potassium chloride (formed from the decomposition of potassium chlorate), which latter dissolves in the water. The crucible is then removed, and carefully washed into the beaker.

The liquid is then filtered, taking care that all the manganese dioxide is transferred *quantitatively* to the filter paper. The residue is washed several times with distilled water, dried in an air-oven, and weighed ; the weight will be found to be the same as before.

The filtrate gives a curdy white precipitate of silver chloride, when treated with a solution of silver nitrate—the precipitate is insoluble in nitric acid, but soluble in ammonium hydroxide ; consequently the residue left after the oxygen is set free from potassium chlorate is a *chloride*.

$$AgNO_3 + KCl = AgCl \text{ (white precipitate)} + KNO_3.$$

The residue of manganese dioxide has not undergone any chemical change.

It may be used over again to act as a catalyst.

Physical properties.—(i) Oxygen is a colourless, tasteless, and odourless gas which may be condensed to a pale blue liquid and frozen to a blue solid. Liquid and solid oxygen are strongly magnetic.

(ii) Oxygen is slightly soluble in water ; and hence the aquatic animals can live. Oxygen is, however, more soluble than nitrogen in water.

Chemical properties.—Oxygen is a very active element and readily combines with many elements (both metals and non-metals) and compounds, slowly at ordinary temperature and vigorously when heated evolving heat and light.

Combination of substances with oxygen, with evolution of heat and light, is known as combustion.

(i) Oxygen is a supporter of combustion but not combustible. Oxygen supports respiration and is essential to the life of plants and animals.

A glowing chip of wood is introduced into a jar of oxygen ; it is immediately *ekindled* but the gas does not burn.

(ii) **Combustion of non-metals in oxygen.**—Some non-metals such as carbon, sulphur, and phosphorus, burn in oxygen to form *acidic oxides*, i.e., oxides which dissolve in water to form acids.

(a) A piece of glowing charcoal taken in a deflagrating spoon is ntroduced into a jar of oxygen, the charcoal burns brilliantly, producing carbon dioxide. The contents of the jar are then shaken with water ; to a portion of the solution is added a few drops of blue itmus solution, it turns wine-red. The gas formed is, therefore, a *weak acid.* Clear lime water is added to the other portion, it turns milky owing to the formation of white insoluble calcium carbonate :

$C + O_2 = CO_2$; $CO_2 + H_2O = H_2CO_3$ (carbonic acid)

$Ca(OH)_2$ (lime water) $+ CO_2 = CaCO_3$ (calcium carbonate) $+ H_2O$

(b) Feebly burning sulphur, and phosphorus are similarly ntroduced into separate jars of oxygen ; sulphur burns with a bright bluish flame, producing sulphur dioxide, and phosphorus burns with a brilliant white flame, forming dense white cloud of phosphorus pentioxide. When shaken with water the products of ombustion produce acids which turn blue litmus red.

$S + O_2 = SO_2$; $SO_2 + H_2O = H_2SO_3$ (sulphurous acid).

$4P + 5O_2 = 2P_2O_5$; $P_2O_5 + H_2O = 2HPO_3$ (metaphosphoric acid).

$HPO_3 + H_2O = H_3PO_4$ (orthophosphoric acid).

(ii) **Combustion of Metals in Oxygen.**—Some metals when heated burn in xygen to give oxides. These are mostly *basic oxides*, i.e., oxides which react with cids to form salt and water.

(a) Small pieces of sodium and potassium are heated in deflagrating spoons ntil they begin to burn, and then introduced into jars of oxygen, they continue urning with bright yellow and violet flames respectively forming *peroxides* mainly, hich may be dissolved in water producing strongly alkaline solutions which turn d litmus blue :

$2Na + O_2 = Na_2O_2$ (soudim peroxide).
$2Na_2O_2 + 2H_2O = 4NaOH$ (sodium hydroxide) $+ O_2$.
$2K + 2O_2 = K_2O_4$ (potassium tetroxide).
$2K_2O_4 + 2H_2O = 4KOH$ (potassium hydroxide) $+ 3O_2$.

(b) Burning magnesium ribbon, inserted into a jar of oxygen, burns with a inding white light, producing white solid magnesium oxide. A piece of iron wire pped with burning sulphur and inserted in a jar of oxygen burns brilliantly, throwing f a shower of white-hot particles of ferroso-ferric oxide.

$2Mg + O_2 = 2MgO$ (magnesium oxide).
$3Fe + 2O_2 = Fe_3O_4$ (ferroso-ferric oxide).

(iv) **At ordinary temperature.**—Oxygen combines fairly rapidly with the following reagents *in the cold* :

(a) Moist white phosphorus reacts with oxygen to yield phosphorus pentoxide—the reaction is used for removing *traces of* oxygen from inert gases such as nitrogen. Iron rusts in moist air, forming hydrated ferric oxide.

(b) A solution of potassium pyrogallate in caustic potash **absorbs** oxygen and turns black—the reaction is used in *gas analysis.*

(c) Nitric oxide combines with oxygen forming brown fumes of nitrogen peroxide—the reaction is used as a **test** for oxygen.

(d) Oxygen can also oxidise sulphurous acid, ferrous and stannous salts in the cold, as shown by the equations :

$2H_2SO_3$ (sulphurous acid) + O_2 = $2H_2SO_4$ (sulphuric acid).
$4FeSO_4$ (ferrous sulphate) + $2H_2SO_4$ + O_2 = $2Fe_2(SO_4)_3$ + $2H_2O$.
$2SnCl_2$ (stannous chloride) + $4HCl$ + O_2 = $2SnCl_4$ + $2H_2O$.

(e) Colourless solution of cuprous chloride in concentrated hydrochloric acid turns green on exposure to air due to formation of cupric chloride ; ammoniacal solution of cuprous chloride, however, turns blue in air.

$$4CuCl + 4HCl + O_2 = 4CuCl_2 + 2H_2O.$$

Tests.—(i) Oxygen rekindles a glowing chip of wood.

(ii) Oxygen forms reddish brown fumes of nitrogen peroxide with nitric oxide : $2NO + O_2 = 2NO_2$.

Absorbents.—Oxygen is absorbed by : (i) a solution of potassium pyrogallate in caustic potash ; (ii) an acid solution of chromous chloride :

$$4CrCl_2 + 4HCl + O_2 = 4CrCl_3 + 2H_2O.$$

Uses.—Oxygen is used (i) as an *aid to respiration* to patients suffering from breathing difficulties as in pneumonia and carbon monoxide poisoning ; in high altitude aviation ; in submarines ; tunnels, and mountaineering, etc.

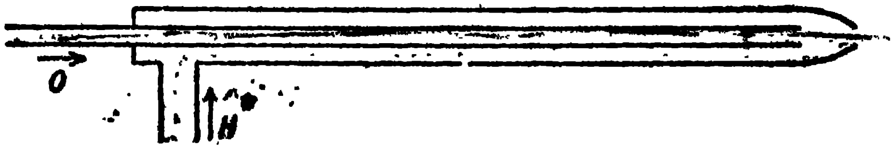


Fig. 57

(ii) in producing oxy-hydrogen and oxy-acetylene flames, much used for cutting and welding metals. An *oxy-hydrogen blowpipe* (fig. 57) consists of two *concentric* tubes ending in jets ; oxygen gas is passed through the inner tube and hydrogen through the outer,—the *mixture* when lighted at the jet produces an intensely hot, pointed flame (temperature about 2800°C) which readily melts platinum.

If the oxy-hydrogen flame impinges on a pencil of quick lime, and intensely white light, called *lime light* is emitted by the incandescent lime. In the *oxy-acetylene blowpipe*, acetylene gas takes the place of hydrogen ; a hotter flame, 3100°—3315°C, suitable for welding and cutting metals such as iron and steel, is obtained.

Liquid oxygen soaked in powdered charcoal has been used as an explosive.

Oxides.—*An oxide is a compound of two elements one of which is oxygen.* The oxides are classified as follows :

(i) **Basic oxides.**—A basic oxide is an oxide which reacts with an acid to yield a salt and water *only* :

MgO (magnesium oxide) + 2HCl = $MgCl_2$ + H_2O.
CuO + H_2SO_4 = $CuSO_4$ (copper sulphate) + H_2O.

Basic oxides are oxides of metals. If soluble in water they produce hydroxides which are also basic. Oxides of alkali metals (sodium, potassium, etc.) and alkaline earths (calcium, barium, etc.) dissolve in water forming soluble hydroxides (called *alkalis*) which turn red litmus blue.

$Na_2O + H_2O = 2NaOH$ (sodium hydroxide).
$CaO + H_2O = Ca(OH)_2$ (calcium hydroxide).
$NaOH + H_2SO_4 = Na_2SO_4$ (sodium sulphate) $+ H_2O$.
$Ca(OH)_2 + 2HCl = CaCl_2$ (calcium chloride) $+ 2H_2O$.

(ii) **Acidic oxides.**—An acidic oxide is an oxide which reacts with a base to yield a salt. Carbon dioxide reacts with sodium hydroxide yielding sodium carbonate :

$CO_2 + 2NaOH = Na_2CO_3$ (sodium carbonate) $+ H_2O$.

Sulphur dioxide yields sodium sulphite on treatment with caustic soda : $SO_2 + 2NaOH = Na_2SO_3$ (sodium sulphite) $+ H_2O$.

An acidic oxide, if soluble, combines with water to yield an acid, and it is, therefore, called *an acid anhydride*.

$P_2O_5 + 3H_2O = 2H_3PO_4$ (phosphoric acid) ; $SO_3 + H_2O = H_2SO_4$

An acidic oxide reacts with a basic oxide to yield a salt :

$CaO + CO_2 = CaCO_3$ (calcium carbonate) ; $Na_2O + SO_3 = Na_2SO_4$

Most of the oxides of non-metals (e.g., CO_2, SO_2, P_2O_5 etc.) and higher oxides of metals (e.g., CrO_3, Mn_2O_7 etc.) are acidic.

(iii) **Amphoteric oxides.**—An amphoteric oxide is one which acts as a weakly basic oxide towards a strong acid and a weakly acidic oxide towards a strong base, i.e., an amphoteric oxide, which is usually a metallic oxide, has both basic and acidic properties.

Zinc oxide reacts with hydrochloric acid to form zinc chloride and water, and hence behave as basic oxide ; but with sodium hydroxide it reacts as an acidic oxide forming sodium zincate :

Basic action : $ZnO + 2HCl = ZnCl_2 + H_2O$. MnO_2, Cr_2O_3
Acidic action : $ZnO + 2NaOH = Na_2ZnO_2$ (sodium zincate) $+ H_2O$.
Aluminium oxide, Al_2O_3 and stannous oxide, SnO, are also amphoteric.

(iv) **Neutral oxides.**—The oxides which are neither acidic nor basic in character are called neutral oxides ; e.g., carbon monoxide, CO ; nitrous oxide, N_2O ; and nitric oxide, NO.

(v) **Peroxides.**—A peroxide of an element contains more oxygen than what is present in its highest *typical acidic or basic oxide*. A *peroxide of a metal yields hydrogen peroxide*, H_2O_2, *on treatment with cold dilute acids :*

Na_2O_2 (sodium peroxide) $+ 2HCl = H_2O_2 + 2NaCl$.

BaO_2 (barium peroxide) $+ H_2SO_4 = H_2O_2 + BaSO_4$.

A peroxide contains the oxygen chain —O—O—, as in sodium peroxide, Na — O — O — Na.

Metallic oxides such as lead dioxide, PbO_2 (usual basic oxide is PbO) and manganese dioxide, MnO_2 (usual basic oxide is MnO) which contain more oxygen than the basic oxides are not peroxides, since they do not yield hydrogen peroxide with dilute acids ; they are described as **polyoxides.** They give oxygen with hot concentrated sulphuric acid, and chlorine with hot and strong hydrochloric acid :

$2MnO_2 + 2H_2SO_4 = 2MnSO_4$ (manganous sulphate) $+ 2H_2O + O_2$.
$MnO_2 + 4HCl = MnCl_2$ (manganous chloride) $+ 2H_2O + Cl_2$.

(vi) **Mixed oxides.**—A mixed oxide is formed by the combination of two simpler oxides. Thus ferroso-ferric oxide, Fe_3O_4, is a mixed oxide of the two basic oxides ferric oxide, Fe_2O_3 and ferrous oxide, FeO. It yields ferric and ferrous chlorides with hydrochloric acid.

$$Fe_3O_4(Fe_2O_3.FeO) + 8HCl = 2FeCl_3 + FeCl_2 + 4H_2O.$$

Oxides of non-metals are always acidic or neutral. Lower oxides of metals are either basic or amphoteric ; higher oxides of metals are often acidic ; e.g., CrO basic, Cr_2O_3 amphoteric, and CrO_3 acidic.

When an element yields more than one oxide, the oxides become more acidic gradually as the valency of the element increases, e.g., MnO strongly basic, Mn_2O_3 basic, MnO_2 amphoteric, MnO_3 acidic, Mn_2O_7 strongly acidic.

Industrial Preparation of Oxygen.—On a technical scale oxygen is obtained —(i) *by the fractional distillation of liquid air*, and (ii) *by the electrolysis of water.*

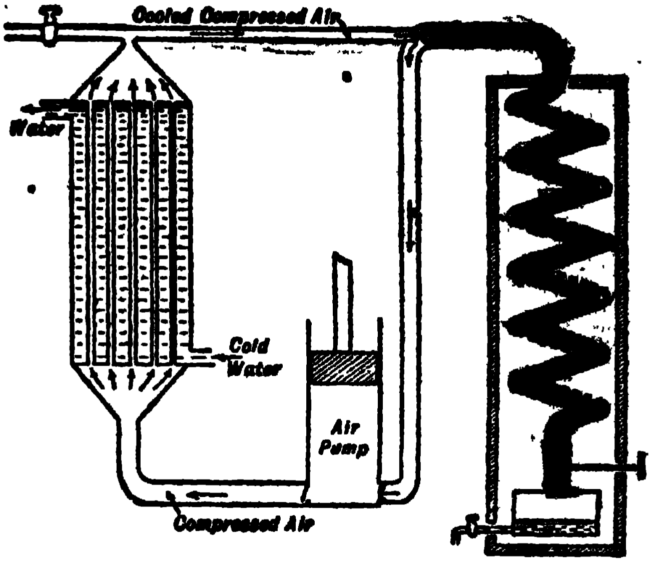


Fig. 58

(i) **Fractional Distillation of Liquid Air.**—Air is a mixture of nitrogen and oxygen mainly, of which the latter forms about 21 per cent by volume. The two gases may be separated by the *liquefaction and fractional distillation of air.* Air is liquefied by subjecting it to high pressure and low temperature. Air is freed from water vapour and carbon dioxide by fused calcium chloride and slaked lime respectively, and then compressed to 200 atmospheres. This heats the air, so it is cooled to ordinary temperature by running water. The compressed air is then pumped down a jacketted spiral tube (fig. 58) and allowed to expand suddenly through a nozzle into a chamber, where it is somewhat cooled by the free expansion (due to Joule-Thomson effect). This cooled air circulates through the jacket *round the spiral* tube, thereby cooling the succeeding stream of incoming compressed air, and is sent back to the compressor—the processes of compression and expansion are repeated. The cooled gas becomes still cooler each time as it suffers expansion till eventually the temperature of incoming air falls below the *critical temperature* when it liquefies. Liquid air (boiling point −190°C) is a mixture of liquid oxygen (b.p. −183°C), and liquid nitrogen (b. p. −196°C). The liquid air is then fractionally distilled. On evaporating liquid air, the evolved vapour become richer in more volatile nitrogen. The separation of nitrogen and oxygen is then effected by allowing the evolved vapours to bubble through liquid air (rich in oxygen) in a tall fractionating column. Nearly pure nitrogen (lower boiling point) leaves the top of the column. The oxygen in the gas condenses and pure liquid oxygen collects at the bottom of the column, which is then evaporated.

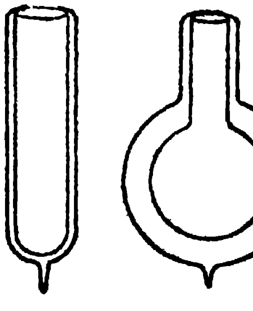


Fig. 59

Liquid air and liquid oxygen may be kept in double-walled glass Dewar (thermos) flasks—there being a high vacuum between the two walls (fig. 59).

A kettle of liquid air boils brisky when kept on a slab of ice.

(ii) **Electrolysis of water.**—Some oxygen is made, together with hydrogen, by the electrolysis of water (see industrial preparation of hydrogen).

Oxygen is stored and transported in steel cylinders, at pressures of 100 atmosphere or so.

Barium monoxide ('baryta') at dull red heat (500°C) absorbs oxygen from air, forming barium peroxide which latter at bright red-heat (800°C) or at reduced pressure gives off oxygen again. This was the principle of Brin's process which is now entirely obsolete.

$$2BaO + O_2 \rightleftharpoons 2BaO_2.$$

Other reactions in which oxygen is liberated.—(i) Oxygen may be obtained very easily (a) by the action of water upon sodium peroxide or *oxone* as it is known technically. Sodium peroxide is taken in a conical flask fitted with a dropping funnel and a delivery tube. On adding water from the dropping funnel oxygen is evolved which may be collected over water : (fig. 60).

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2.$$

Cubes of sodium peroxide, supplied for the preparation of oxygen in a Kipp's apparatus, contain traces of ferric oxide and copper sulphate, to catalyse evolution of oxygen.

(b) by the action of hydrogen peroxide upon a mixture of dilute sulphuric acid and potassium permanganate : pure oxygen is evolved on dropping hydrogen peroxide solution into a solution of potassium permanganate in dilute sulphuric acid in the conical flask (fig. 60). The oxygen is collected over water ; the pink solution becomes colourless.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

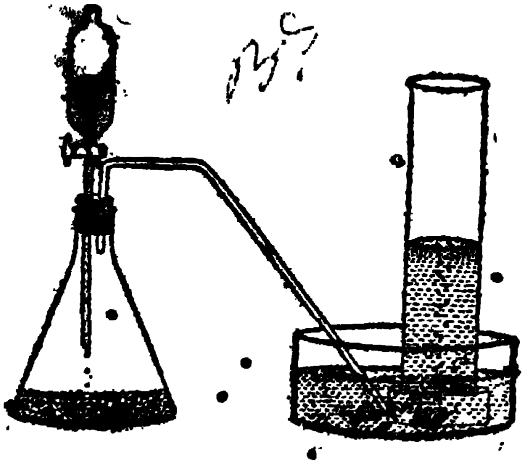


Fig. 60

(ii) Oxygen is also liberated by the thermal decomposition of the oxide of feebly electro-positive metals, such as silver oxide and mercuric oxide, and most higher oxides and peroxides, such as PbO_2, CrO_3, BaO_2, etc.

Mercuric oxide decomposes on strong heating into mercury and oxygen :

$$2HgO \rightleftharpoons 2Hg + O_2.$$

The reaction was used by Lavoisier *to abstract oxygen from air ;* when heated in air, mercury forms *mercuric oxide* which decomposes at a higher temperature into mercury and oxygen. Silver oxide decomposes at a lower temperature than mercuric oxide and gives *very pure* oxygen : $2Ag_2O = 4Ag + O_2$.

Barium peroxide decomposes into barium monoxide (baryta) and oxygen : $2BaO_2 \rightleftharpoons 2BaO + O_2$. Both red lead, Pb_3O_4, and lead dioxide, PbO_2, evolve oxygen on heating : $2Pb_3O_4 = 6PbO + O_2$; $2PbO_2 = 2PbO + O_2$.

Chromium trioxide breaks up on heating into chromic oxide and oxygen ; manganese dioxide decomposes at *bright-red heat,* evolving oxygen :

$$4CrO_3 = 2Cr_2O_3 + 3O_2 ; \quad 3MnO_2 = Mn_3O_4 + O_2.$$

(iii) **Oxy-acids and their salts.**—Many oxy-salts, such as chlorates, and nitrates, etc., and the oxy-acids, such as sulphuric acid and nitric acid, etc., decompose when heated.

(a) Potassium nitrate, also known as *nitre* or *saltpetre*, decomposes on heating into potassium nitrite and oxygen, sodium nitrate behave similarly. Potassium permanganate $KMnO_4$, and potassium dichromate $K_2Cr_2O_7$, also decompose on heating, giving off oxygen :

$2KMnO_4 = K_2MnO_4$ (potassium manganate) $+ MnO_2 + O_2$.
$4K_2Cr_2O_7 = 4K_2CrO_4$ (potassium chromate) $+ 2Cr_2O_3 + 3O_2$.
$2KNO_3$ (potassium nitrate) $= 2KNO_2$ (potassium nitrite) $+ O_2$.

(b) A paste of bleaching powder when heated with a few drops of cobalt chloride solution rapidly evolves oxygen—the cobalt chloride acts as a catalyst :

$$2Ca(OCl)Cl = 2CaCl_2 + O_2.$$

(c) When dry powdered lead nitrate is strongly heated in a hard glass test tube (figure 61), it decomposes into yellow lead monoxide PbO, and a mixture of gas, nitrogen dioxide and oxygen—nitrogen dioxide forms reddish brown fumes. The gas evolved is passed through a U-tube cooled in a mixture of ice and common salt, where nitrogen peroxide condenses to a yellow liquid, and oxygen passes out. A glowing splint held over the exit of the U-tube bursts into flame, showing that oxygen is evolved :

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

(d) When strong nitric acid is allowed to fall upon red-hot pumice stone, it decomposes into water, nitrogen peroxide and oxygen :

$$4HNO_3 = 2H_2O + 4NO_2 + O_2.$$

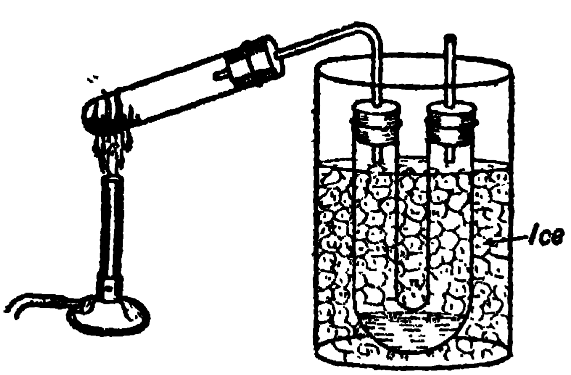


Fig. 61

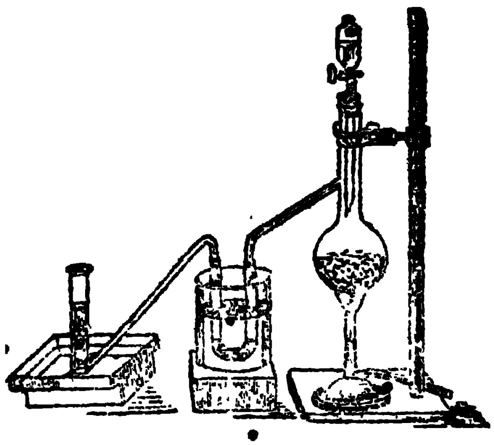


Fig. 62

A distilling flask containing some, pumice-stone, is fitted with a dropping funnel, and a delivery tube *via* a U-tube cooled in freezing mixture. The flask is strongly heated, and strong nitric acid is allowed to fall by drops on the hot pumice-stone (fig. 62).

The evolved gas is passed through the U-tube where the nitrogen peroxide condenses to a liquid, and oxygen passes out—the gas is collected over water.

(c) Strong sulphuric acid may be similarly decomposed by allowing to drop on red-hot pumice-stone, into water, sulphur dioxide, and oxygen, the mixed gases on being sent through the U-tube, as before, SO_2 condenses to liquid and oxygen passes out :

$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2.$$

Hydrogen

Atomic number 1. Atomic weight 1.008. Melting point −259°C. Boiling point −252.7°C. Density, 1 litre at 0°C and 760 mm. weighs 0.0899 gm.

History and occurrence.—Hydrogen was first prepared by Boyle in 1660 from iron filings and dilute mineral acids ; but it was carefully investigated by Cavendish in 1766 and called by him *inflammable air.* He also showed it to be a constituent of water (1781—84), a fact in virtue of which Lavoisier gave it the name *hydrogen* or 'water producer' in 1783.

In the free state hydrogen occurs in many volcanic and other natural gases, in the atmosphere of the sun, and in air in traces (about 1 part per million) only. In the combined state it is present in oils, fats, wood, coal, petroleum, water, etc.

Preparation.—The chief sources of hydrogen are—(i) *acids,* (ii) *water,* and (iii) *alkalis.*

Hydrogen from acids.—Hydrogen is obtained from acids by interaction with metals which are more electro-positive than hydrogen.

Metals above hydrogen (with the exception of lead) in the electro-chemical series (page 130) displace hydrogen from acids, such as hydrochloric acid and sulphuric acids—the higher the metal in the series the more vigorous the displacement. The feebly electropositive metals like Cu, Hg, Ag, Au and Pt do not react. Only 12 metals are shown in the series here :

Hydrogen is easily liberated by the action of dilute hydrochloric or sulphuric acid upon iron, magnesium and zinc or by the action of hot and strong hydrochloric acid upon tin :

$$Fe + 2HCl = FeCl_2 \text{ (ferrous chloride)} + H_2,$$
$$Fe + H_2SO_4 = FeSO_4 \text{ (ferrous sulphate)} + H_2.$$
$$Mg + H_2SO_4 = MgSO_4 \text{ (magnesium sulphate)} + H_2,$$
$$Sn + 2HCl = SnCl_2 \text{ (stannous chloride)} + H_2.$$

Laboratory preparation.—Hydrogen is usually prepared in the laboratory by the action of dilute sulphuric acid (1 volume concentrated acid to 5 volumes water) or hydrochloric acid (1 volume concentrated acid to 2 volumes water) on granulated zinc :

K
Na
Ca
Mg
Al
Zn
Fe
Sn
Pb
H
Cu
Hg
Ag

$$Zn + 2HCl \text{ (hydrochloric acid)} = ZnCl_2 \text{ (zinc chloride)} + H_2.$$
$$Zn + H_2SO_4 \text{ (sulphuric acid)} = ZnSO_4 \text{ (zinc sulphate)} + H_2.$$

A few pieces of granulated zinc are put under water in a two-necked *Woulfe's bottle* tightly fitted with corks through one of which passes a thistle funnel reaching down very nearly to the bottom and through the other passes the delivery tube which dips under water in a pneumatic trough (fig. 63). The apparatus must be perfectly **air-tight,** *since hydrogen forms an explosive mixture with air.* To test this, air is blown from the mouth through a rubber tube attached at the free end of the delivery tube when water is forced up the stem of the funnel. The apparatus is air-tight, if the water level in the funnel remains stationary after closing the rubber tubing by pressing hard with fingers.

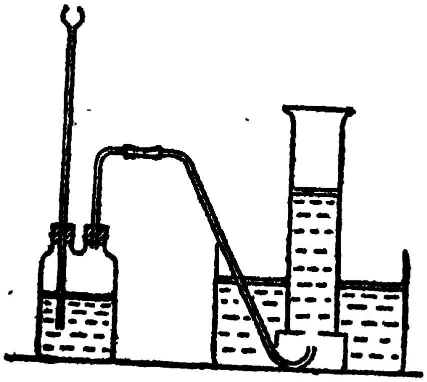


Fig. 63

Moderately strong sulphuric acid is then poured down the funnel, when a brisk reaction sets in with the rapid evolution of hydrogen. The gas is allowed to escape for a minute or two to drive out the air inside the bottle. To ensure this, a sample of the gas is collected in a test tube by the displacement of water and brought near the flame. When the gas burns *quietly*, it is free from air and is ready for collection. To collect the gas, a gas jar, completely filled with water and closed with a greased cover glass, is inverted over water in the trough ; while under water, the cover glass is removed and the gas jar is placed on the shelf of the trough so that the delivery tube reaches the mouth of the jar through an opening in the shelf. Hydrogen collects in the jar *by the displacement of water.* When the jar is full of the gas, its mouth is closed with a glass plate, while still under water, and it is then removed from the trough. The jar is kept *with its mouth downwards*. Several jars of hydrogen are similarly collected to study its properties. The gas may be dried by passing through a U-tube containing calcium chloride or phosphorus pentoxide and collected over mercury.

Before collecting hydrogen all the air must be displaced from the apparatus, since hydrogen forms an explosive mixture with air.

Physical properties.—(i) Hydrogen is a colourless, tasteless and odourless gas which is practically *insoluble* in water. The gas may be condensed only with difficulty to a liquid and frozen to a solid which *does not exhibit metallic properties.*

(ii) Hydrogen is the *lightest* of all substances. Air is 14.4 times heavier than hydrogen. The following experiments show that *hydrogen is lighter than air :*

Expt.—(a) An 'empty' gas jar (i.e., full of air) is inverted over a jar of hydrogen, and the cover glass from the mouth of the latter is then removed. After a few seconds when a lighted taper is applied to the mouth of the upper jar, it is found that the gas burns there with a slight explosion—hydrogen *being lighter than air has travelled to upper jar* (fig. 64).

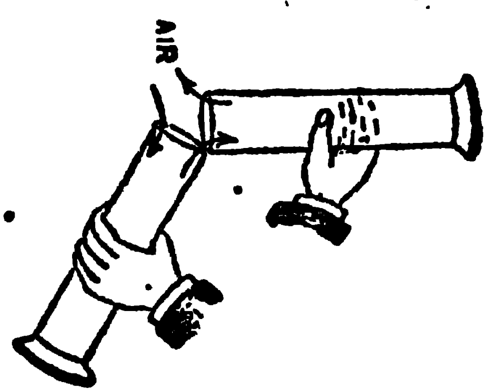


Fig. 64

Expt.—(b) A toy rubber balloon is filled with hydrogen until it is sufficiently inflated ; it is then tied off with a loop of of thread and released in air—the balloon rises up in the air.

Chemical properties.—(i) Hydrogen does not support combustion, but burns in air or oxygen with a pale blue non-luminous flame.

Expt.—A lighted taper is introduced into a jar of hydrogen, held mouth downwards—the taper is extinguished but the gas burns with a pale blue flame.

(ii) *Water is produced when hydrogen burns in air or oxygen.* This reaction is used as a test for hydrogen. $2H_2 + O_2 = 2H_2O$.

Expt.—A stream of hydrogen, dried by passing through a U-tube containing fused calcium chloride, is burnt in a platinum jet, and the flame is allowed to impinge on the outer surface of a retort (fig. 65) through which cold water circulates. Drops of water condense on the cold outer surface and collect in a beaker placed below.

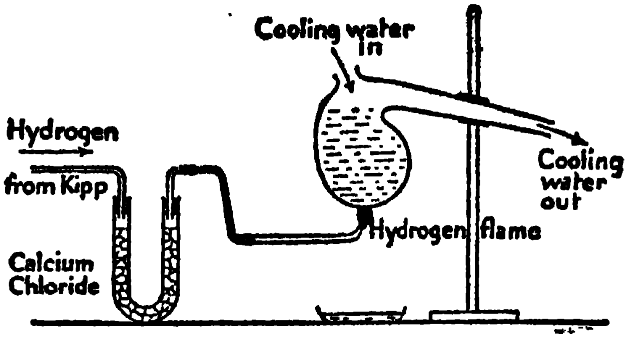


Fig. 65

The reaction between hydrogen and oxygen is catalysed by finely-divided platinum and palladium—a jet of hydrogen inflames, for example, in contact with platinum sponge and fine platinum wire, although hydrogen and oxygen do not react at the ordinary temperature. The combination is however arrested by *completely drying* the gases with phosphorus pentoxide.

When glass tubes of different widths and lengths are lowered over the flame, a musical note is produced and the flame begins to sing.

(iii) *Hydrogen forms an explosive mixture with air or oxygen.*

Expt.—A soda water bottle is filled one-third its volume with oxygen and two-thirds by hydrogen, by displacement of water ; the bottle is wrapped with a towel, and well-shaken, and then held before a flame when a violent explosion takes place instantaneously.

(iv) *Hydrogen acts as a reducing agent,* because of its tendency to unite with oxygen.

Expt.—Hydrogen is passed over heated copper oxide taken in a bulb-tube (fig. 66)—the *black* copper oxide is converted into metallic copper with *dull-red* colour and water is formed. (Also see page 76). Hydrogen here acts as a reducing agent, since it removes the oxygen from copper oxide—the removal of oxygen from a compound being called reduction.

$$CuO + H_2 = Cu + H_2O \; ;$$
$$PbO + H_2 = Pb + H_2O.$$

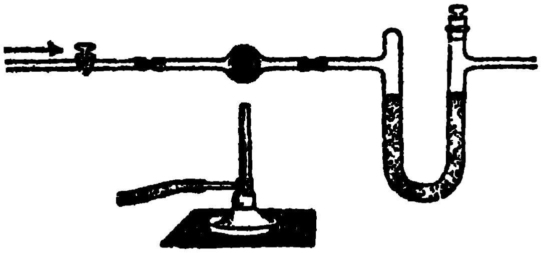


Fig. 66

Oxides of weakly electro-positive metals like mercury, iron, lead, etc., may be similarly reduced. Hydrogen does not attack the oxides of strongly electro-positive metals like sodium, potassium, calcium or magnesium.

(v) Hydrogen forms gaseous or volatile hydrides with all the non-metals, except the inert gases :

$H_2 + Cl_2 = 2HCl$ (hydrochloric acid) ; $3H_2 + N_2 = 2NH_3$ (ammonia).

(vi) Hydrogen forms solid *salt-like hydrides* with strongly electro-positive metals like lithium, sodium, potassium, and calcium—the hydrides react with water producing hydrogen back :

$Ca + H_2 = CaH_2$ (calcium hydride) ; $2Na + H_2 = 2NaH$.

$CaH_2 + 2H_2O = Ca(OH)_2$ (calcium hydroxide) $+ 2H_2$.

Calcium hydride is called **hydrolith** and is sometimes used to prepare hydrogen on a semi-technical scale.

Occlusion of hydrogen.—Hydrogen possesses the property of dissolving in certain metals forming *solid solutions ;* this phenomenon is known as occlusion of hydrogen. Metals like iron, cobalt, platinum and specially palladium possess the property of absorbing a large volume of hydrogen at the ordinary temperature. Of all the metals, palladium absorbs hydrogen the most—about 900 times its own volume. The occluded hydrogen is released again when the metal is heated—use being made of this fact *in the purification of hydrogen.*

Occluded hydrogen is a powerful reducing agent. When *hydrogenised palladium*, for example, is immersed in a solution of ferric chloride, the latter is reduced to ferrous chloride.

Nascent hydrogen.—Nascent hydrogen is *hydrogen at the moment of its generation*, i.e., when it is just liberated from a compound. Nascent hydrogen is *more reactive and a more powerful reducing agent* than ordinary hydrogen, as the following experiments will show :

Expt. (i).—When zinc and sulphuric acid are added to *yellow* solution of ferric chloride, the latter is rapidly reduced to a *colourless* solution by the nascent hydrogen generated within it :

$$FeCl_3 \text{ (ferric chloride)} + H = FeCl_2 \text{ (ferrous chloride)} + HCl.$$

Expt. (ii).—When a little potassium permanganate, $KMnO_4$, solution is added to a mixture of zinc and sulphuric acid which is evolving hydrogen, the *pink* colour of the solution gradually disappears due to the reduction of the permanganate by nascent hydrogen ; but no change is produced when hydrogen is bubbled through the solution of potassium permanganate or ferric chloride.

$$5Zn + 5H_2SO_4 = 5ZnSO_4 + 10H \text{ (nascent hydrogen).}$$

$$\begin{aligned} \text{By partial equations, } 2KMnO_4 &= K_2O + 2MnO + 5O \\ K_2O + H_2SO_4 &= K_2SO_4 + H_2O \\ 2MnO + 2H_2SO_4 &= 2MnSO_4 \text{ (manganous sulphate)} + 2H_2O \\ 10H + 5O &= 5H_2O \end{aligned}$$

$$2KMnO_4 + 3H_2SO_4 + 10H = K_2SO_4 + 2MnSO_4 + 8H_2O$$

Several explanations of the enhanced activity of nascent hydrogen have been put forward, namely : (1) the nascent hydrogen is *in the atomic state*, and the atoms are more active than molecules. Following facts lend support to the atomic character of nascent hydrogen. Langmuir showed that atomic hydrogen reacts directly with oxygen to give hydrogen peroxide.

$$H + O_2 + H = HO - OH$$

(ii) the nascent hydrogen is evolved in small bubbles containing the gas at high pressure ; hydrogen under pressure reduces silver nitrate solution ; and (iii) the nascent hydrogen is activated by the energy liberated in the reaction in which it is formed. This hypothesis has the merit of explaining the difference in activity of nascent hydrogen obtained from different sources. Potassium chlorate, for example, is reduced by nascent hydrogen from zinc and sulphuric acid, but is unaffected by nascent hydrogen from sodium amalgam and water. Since chemical changes which liberate hydrogen, take place with the liberation of different amounts of energy, the nascent hydrogen is energised to different extents in different cases. This explains the difference in activity.

Hydrogen from water.—Hydrogen may be obtained from water (i) *by electrolysis*, and (ii) *by the action of metal*, and (iii) *by the action of carbon.*

(i) **Electrolysis of water.**—*Acidulated water is decomposed by electrolysis into 2 volumes of hydrogen and 1 volume of oxygen ;* (page 11).

(ii) **The action of metal upon water.**—Metals above hydrogen in the electro-chemical series, except tin and lead, decompose water, giving off hydrogen. The conditions under which water is decomposed by metals depend upon the nature of the metal.—(a) **Action of metals upon cold water.**—Alkali metals (sodium, potassium, etc.) and the alkaline earth metals (calcium, strontium and barium) decompose water *at the ordinary temperature*, yielding hydrogen and the hydroxide of the metals which dissolve in the water.

The reaction with alkali metals is very violent ; it can be moderated by alloying the metal with lead or using an amalgam (alloy with mercury) of the metal.

When small pieces of sodium or potassium are thrown in cold water, they swirl about and gradually dissolve, giving off hydrogen ; in the case of potassium so much heat is generated that the evolved hydrogen ignites and a beautiful violet flame appears.

$$2Na + 2H_2O = 2NaOH \text{ (sodium hydroxide) } + H_2.$$
$$2K + 2H_2O = 2KOH \text{ (potassium hydroxide) } + H_2.$$
$$Ca + 2H_2O = Ca(OH)_2 \text{ (calcium hydroxide) } + H_2.$$

Expt.—To collect hydrogen from the reaction of sodium and water, the metal, in small pieces, is held under water with a wire gauze spoon, or pressed into a lead tube, and placed beneath an inverted jar of water. Hydrogen collects in the jar by the displacement of water. The water reacts alkaline *due to the solution of sodium hydroxide* produced in the reaction.

Amalgamated aluminium is made by rubbing aluminium foil with moist mercuric chloride. Zinc-copper couple is made by pouring copper sulphate solution over granulated zinc and washing the product free from adhering salts.

$$CuSO_4 + Zn = ZnSO_4 + Cu$$

(b) **Action of metals upon boiling water.**—The metals magnesium and aluminium in the form of powder or as amalgam, and zinc coated with copper (since *pure zinc is not acted upon by water*) decompose boiling water, liberating hydrogen.

$$Zn + 2H_2O = Zn(OH)_2 \text{ (zinc hydroxide) } + H_2.$$
$$2Al + 6H_2O = 2Al(OH)_3 \text{ (aluminium hydroxide) } + 3H_2.$$

Magnesium and aluminium amalgams also decompose cold water slowly.

(c) **Action of heated metals upon steam.**—Hydrogen is liberated when steam is passed over red-hot iron, zinc or magnesium. Magnesium burns brightly when heated in steam.

$$Mg + H_2O = MgO \text{ (magnesium oxide) } + H_2.$$
$$Zn + H_2O = ZnO \text{ (zinc oxide) } + H_2.$$
$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 \text{ (ferroso-ferric oxide) } + 4H_2.$$

A piece of *weldless* iron pipe is loosely packed with iron filings or small iron nails and heated to redness in a furnace ; on passing steam over the red-hot iron, bubbles of gas are evolved from the delivery tube, which may be collected over water and shown to be hydrogen (fig. 67).

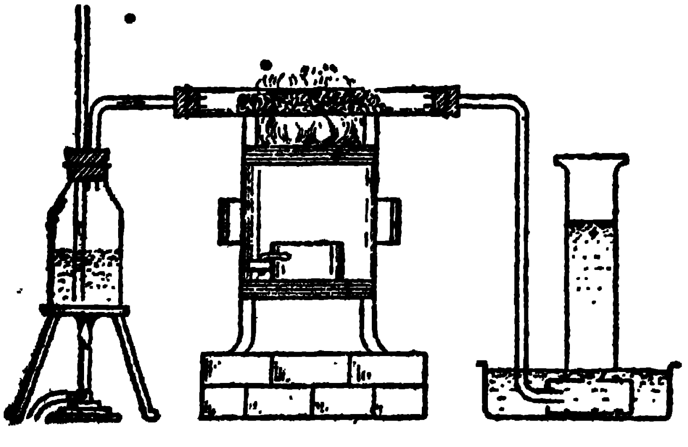


Fig. 67

(iii) **Action of carbon on water.**—A mixture of carbon monoxide and hydrogen, (nearly in equal volumes), called **water gas,** is produced when steam is passed over white-hot carbon heated to 1000°C—much carbon dioxide is produced at dull-red heat :

$$C + 2H_2O = CO_2 + 2\ H_2\ \textit{(dull-red heat)}\ ;$$

$$C + H_2O = CO + H_2\ \textit{(bright-red heat)}.$$

Hydrogen from alkalis.—Hydrogen may be obtained by heating the metals zinc, tin or aluminium, with 20 to 30 per cent caustic soda or potash solution in a flask—the gas may be collected over water.

$$Zn + 2NaOH = Na_2ZnO_2 \text{ (sodium zincate) } + H_2.$$

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 \text{ (sodium aluminate) } + 3H_2.$$

$$Sn + 2NaOH = Na_2SnO_2 \text{ (sodium stannite) } + H_2.$$

In the **silicol process** hydrogen is made for filling military balloons by the action of hot 20% caustic soda solution upon powdered silicon or ferrosilicon containing about 80% silicon.

Hydrogenite (which is a mixture of silicon, caustic soda and slaked lime) evolves hydrogen on ignition and leaves sodium and calcium silicates.

$$Si + 2NaOH + H_2O = Na_2SiO_3 \text{ (sodium silicate) } + 2H_2.$$

Tests for Hydrogen.—Hydrogen burns in oxygen with a pale blue flame to form water *only*—the product of combustion, i.e., water, does not make lime water milky, but turns *white* anhydrous copper sulphate *blue.*

Hydrogen is absorbed by spongy palladium which gives off the gas again on heating.

Uses.—Hydrogen is used industrially : (i) in the manufacture of ammonia, hydrochloric acid, and methyl alcohol ;

(ii) for hydrogenating petroleum fractions, and coal in order to obtain synthetic petrol ;

(iii) in the hydrogenation, also called *hardening*, of vegetable or animal oil—the oil combines with hydrogen in presence of finely divided nickel catalyst, forming solid fats, which are used extensively as butter substitutes ;

(iv) in producing oxy-hydrogen flame, temperature about 2800°C, for welding and lime light—lead 'burning', i.e., autogenous welding without solder is done by a hydrogen flame ; a still hotter flame, temperature about 4000°C, is produced in *atomic hydrogen* torches, also used for welding purposes.

Atomic Hydrogen.—The molecule of hydrogen can be split into atoms—the process absorbing a huge amount of energy, about 100,000 cals. per molecule : $H_2 \leftrightharpoons 2H$. Atomic hydrogen is formed when an electric arc between tungsten electrodes is fed with hydrogen—the atomic hydrogen blown out of arc forms an intensely hot flame capable of melting and welding many metals. The flame gets its heat from the reunion of hydrogen atoms to molecules : $2H \leftrightharpoons H_2$. Atomic hydrogen is also a powerful reducing agent.

(v) in filling air-ships and balloons, since it is the lightest gas known, its density relative to air = 1, is 0.069 only. Coal gas is sometimes used for balloons as it contains a large proportion of hydrogen, and for airships hydrogen is often replaced now-a-days by non-inflammable helium (having a lifting power of 92 per cent of that of hydrogen) as the inflammability of hydrogen makes its use extremely risky.

Pure Hydrogen.—(i) Hydrogen, obtained from commercial zinc and sulphuric acid contains many impurities, such as hydrogen sulphide, H_2S, arsine, AsH_3, phosphine, PH_3, sulphur dioxide, carbon dioxide, possibly oxides of nitrogen, nitrogen, and moisture. The gas is purified by passing it in succession through a series of U-tubes containing :

(a) lead nitrate solution to absorb hydrogen sulphide,
(b) silver sulphate solution to absorb arsine and phosphine,
(c) strong caustic potash solution to absorb sulphur dioxide, carbon dioxide, and nitrogen dioxide ;
(d) phosphorus pentoxide to absorb moisture.

The gas may be then collected over mercury. *To remove nitrogen,* the gas is passed in an evacuated glass bulb containing palladium foils which absorb hydrogen *only*—the nitrogen is pumped out of the bulb. Pure hydrogen is then evolved by heating the bulb to dull-redness.

(ii) Very pure hydrogen is prepared in the laboratory by the electrolysis of a warm barium hydroxide solution in a glass U-tube, fitted with nickel electrodes (fig. 68). Water undergoes electrolysis, liberating hydrogen at the cathode and oxygen at the anode—barium hydroxide increases the conductivity of the solution only. The hydrogen, thus liberated, contains a trace of oxygen, and is therefore *passed over heated platinised asbestos to convert the oxygen into water.* Moisture is then removed by drying the gas with potassium hydroxide, followed by phosphorus pentoxide. The gas is then collected over mercury.

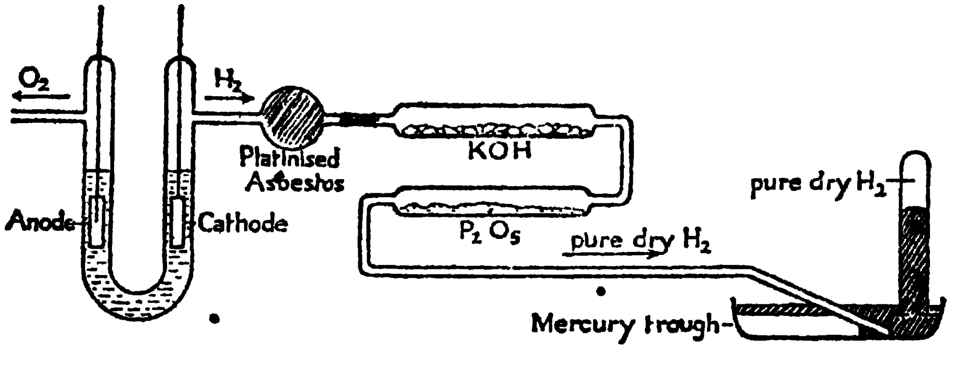


Fig. 68

Industrial preparation of hydrogen.—The principal processes for the manufacture of hydrogen are (i) *electrolytic process*, (ii) *water gas process*, and (iii) *steam-iron process.*

(i) **Electrolytic process.**—Hydrogen is obtained in Knowles cells by the electrolysis of a 20% caustic soda solution in a cast iron tank between sheet-iron electrodes. The anodes, (which are nickel-plated to resist anodic oxidation) and cathodes are placed alternately. Each electrode is fitted with a gas collecting bell at the top ; the electrodes are separated from each other by porous asbestos diaphragm to prevent the hydrogen evolved at the cathode from mixing with the oxygen liberated at the anode, since the diffusion and intermixture of hydrogen and oxygen would form an explosive mixture. The purity of gases is very high—H_2 99.9% and O_2 99.6%. High purity hydrogen is required for synthesis of ammonia and for hardening of oils.

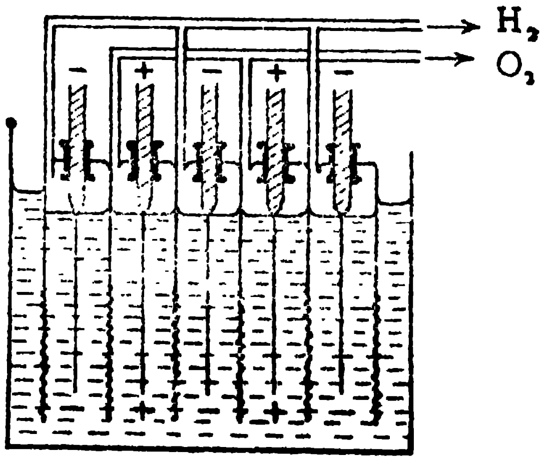


Fig. 69

Hydrogen is obtained as a by-product during the manufacture of caustic soda by the electrolysis of common salt.

(ii) **Water gas process.**—When steam is passed over white-hot coke heated to about 1000°C water gas is produced—a mixture of nearly equal volumes of hydrogen and carbon monoxide with a small amount of carbon dioxide : $C + H_2O = CO + H_2$.

In **Bosch process** the water gas is mixed with excess of steam and passed at 450°C over a heated catalyst consisting of a mixture of ferric oxide and chromium oxide ; carbon monoxide is mostly oxidised into carbon dioxide and more hydrogen is obtained from the steam $CO + H_2O \rightleftharpoons CO_2 + H_2$. As the reaction is *reversible,* a little carbon monoxide always remain in the gas.

The carbon dioxide is removed from the gas mixture by washing with a spray of water under a pressure of 30 atmospheres, and any remaining carbon monoxide by absorption in ammoniacal cuprous formate solution under 200 atmospheres. The hydrogen, when dried, is about 99.9 % pure.

Carbon monoxide can also be removed from water gas by compression and strong cooling, when carbon monoxide (b.p. −191.5°) condenses to a liquid, leaving the hydrogen (b.p. −253°) as a gas.

Hydrogen is made in California by the thermal decomposition of natural gas, which is methane mainly : $CH_4 = C + 2H_2$ or the natural gas is mixed with steam and heated : $CH_4 + 2H_2O = CO_2 + 4H_2$.

(iii) **Steam-iron process.**—Hydrogen is made by passing steam over red-hot iron. In the *Lane process* spongy iron obtained from the reduction of spathic iron ore (ferrous carbonate) is heated to about 600°—850°C in vertical iron retorts, and steam is passed over it. The red-hot iron decomposes steam, liberating hydrogen, and is itself converted to ferroso-ferric oxide : $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$.

The iron oxide is then reduced back to metallic iron by passing water gas over it, so that the iron can be used over again.

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O \ ; \ Fe_3O_4 + 4CO = 3Fe + 4CO_2.$$

The steaming and reduction processes alternate. The hydrogen obtained is 98 p.c. pure—it contains a little carbon monoxide.

Hydrogen is sometimes made for filling military balloons : (i) by the action of water on calcium hydride (*hydrolith*) or an alloy of lead and sodium (*hydrone*) or (ii) by *silicol process,* as stated above.

The Kipp's apparatus.—To get a ready and fairly continuous supply of hydrogen for occasional use Kipp's apparatus (fig. 70) is conveniently used. It consists of two parts—(i) the lower part of two globes, the lowest being a half only, joined by a narrow neck, (ii) the upper part is another glass globe A with a long stem and fitting air-tight into the neck of the middle globe B,—the stem reching nearly the bottom of the lowest globe. A stop-cock is attached to the central globe. The bottom globe C is provided with an outlet for the escape of the waste liquid.

Pieces of granulated zinc are placed in the central globe B. The stop-cock is opened and dilute sulphuric acid is poured in through a funnel down the upper globe until it fills the bottom globe C and comes in contact with the zinc in the central globe. The reaction takes place between the zinc and the acid. Hydrogen is evolved and passes out through the stop-cock.

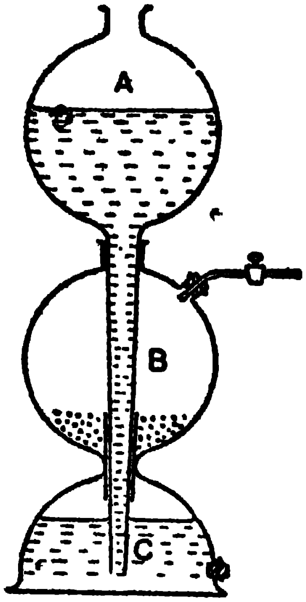


Fig. 70

When the gas is not required, the stop-cock is closed ; the evolved gas cannot pass out ; it collects in the central globe and exerts pressure on the acid liquid which is thereby forced down into the bottom globe whence it rises up the stem into the top globe. The contact between the zinc and the acid breaks and consequently the evolution of hydrogen ceases.

When the gas is wanted, the stop-cock is opened ; the accumulated gas escapes and so the pressure inside falls and the acid as a result comes down in contact with zinc again and the gas is evolved.

The Kipp's apparatus is used whenever a gas is obtained by the action of a liquid upon a solid *without application of heat*—hence its use also for the ready supply of hydrogen sulphide, carbon dioxide, etc.

Water

Formula H_2O. Molecular weight 18. Freezes at 0°C and boils at 100°C at standard atmospheric pressure. Density at 4°C is unity. Critical temperature 365°C. Volume of 1 kilogram of water at 4°C is the standard litre ; it occupies 1000 ml.

History and Occurrence.—Water for a long time was regarded as an element —the elements, according to the ancient philosophers, being five in number only, namely, fire, air earth, water and ether. It was only in the year 1781 that water was shown to be a compound by Cavendish who obtained it by exploding a mixture of hydrogen and oxygen in the ratio of 2 to 1 by volume.

Water occurs abundantly in nature as liquid water or ice in oceans and inland waters, and as vapour in the atmosphere. Water is an important constituent of all animal and vegetable bodies. It also occurs as water of hydration in many rocks and minerals.

Natural waters.—Natural waters contain many impurities—their nature and amounts varying with the source of water. Hence water may be classified according to their sources, as : (a) rain water, (b) river water, (c) spring and well-water, (d) mineral waters, and (e) sea water.

(a) **Rain water.**—The purest form of natural water is rain *water*. It contains in solution the gaseous impurities oxygen, nitrogen and carbon dioxide absorbed from the atmosphere, and traces of ammonium nitrate, produced during thunderstorms, and common salt derived from dried sea spray carried inland by winds. Rain water in the vicinity of manufacturing towns is also liable to contain traces a little sulphur, and many suspended impurities like soot and dust. *The rain water is soft.*

(b) **River water.**—Rain waters feed rivers. Hence the river water contains additional impurities dissolved out from the soil and rocks—the impurities frequently include the chlorides, sulphates, carbonates and bicarbonates of sodium, calcium, magnesium and iron. The soluble bicarbonates of calcium and magnesium are formed by the action of dissolved carbon dioxide upon insoluble carbonates, as the water flows down and through the rocky soil containing calcium or magnesium carbonates.

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2 \text{ (calcium bicarbonate).}$$

$$MgCO_3 + H_2O + CO_2 = Mg(HCO_3)_2 \text{ (magnesium bicarbonate).}$$

The presence of soluble calcium and magnesium salts in river water makes it *hard.* The river water is often liable to be contaminated with the sewage and sludges of cities it flows by, and is then likely to contain organic matter, ammonia and nitrites.

(c) **Spring and well-water.**—The rain water, on reaching the ground, percolates through the porous starta of the soil—this natural filtration through the porous strata removes the suspended impurities but increases the soluble mineral content.

The spring water is usually hard and also free from organic matter, ammonia, etc., as they are oxidised by soil bacteria. Because of freedom from organic matter, the spring and well water is often suitable as drinking water.

The spring water often contains an excess of mineral matter which confers a special taste or a specific curative and medical property to it ; it is known as *mineral water.* There are different types of mineral water (*a*) *Acidulous water,* e.g., Seltzer water, contain dissolved carbon dioxide mainly ; (*b*) *Alkaline water,* e.g., Vichy water, contains sodium and lithium bicarbonates, and are beneficial in the treatment of gout ; (*c*) *Bitter waters,* e.g., Epsom water, contain an excess of sodium and magnesium sulphates, and are used as aperient ; (*d*) *Hepatic waters* contain hydrogen sulphide, and alkali sulphide ; (*e*) *Chalybeate* or *Ferruginous waters* contain ferrous bicarbonate in solution ; (*f*) *Iodine waters* contain dissolved iodides, and (*g*) *Siliceous waters* contain dissolved silica and alkaline silicates.

Hot springs are often used for medicinal bath, they contain dissolved gases like helium and traces of radium emanation.

(d) **Sea water.**—Rivers carry a large volume of waters with dissolved impurities into the sea, and as such the sea contain the maximum amount of dissolved impurities, about 3.6% on the average, of which 2.6% is common salt. The high ratio of sodium to potassium in sea water is partly due to the fact that the soil preferentially retains potassium salts. The average percentage composition of sea water is : water 96.5, sodium chloride 2.6, magnesium chloride 0.3, magnesium sulphate 0.2, calcium sulphate 0.13, potassium chloride 0.07, magnesium bromide 0.007, and the rest traces of silica, iodides, etc. Its specific gravity is 1.03, which one feels while swimming in sea water which buoys up human body better than river water. The quantity of dissolved salts is very much greater in inland seas, e.g., the Dead Sea contains 22.8 per cent of dissolved salts. It is saline and unsuitable as drinking water and is hard.

Hard and soft waters.—Water is classed as hard or soft, depending upon its behaviour towards soap solution. Water that readily forms a lather of films and froths when agitated with a soap solution is known as *soft water,* while the water that reacts with the soap solution to form a white scum only without producing a lather easily, is said to be *hard water*—hard water does not, therefore, yield a lather until a considerable amount of soap has been used up.

The hardness of water is due to the presence of dissolved salts of metals (except the salts of alkali metals such as sodium and potassium), notably those of calcium, magnesium and iron, in water.

The surface tension of water is considerably lowered by the presence of soap in solution. Stable lather of films and froths are therefore formed, when water is shaken with soap solution.

Ordinary soaps consist of sodium and potassium salts of certain fatty acids, such as salts of stearic acid, palmitic acid, and oleic acid derived from fats and oils ; they are soluble in water. When hard water is treated with a soap solution, the soluble sodium stearate (sodium stearate representing the soap) reacts with the calcium, magnesium and iron salts present in hard water to yield insoluble slimy precipitates of the stearates of calcium, magnesium and iron. Soap is thus removed from water.

$$\text{Na-stearate} + \text{Ca-salt} = \text{Ca-stearate} + \text{Na-salt}.$$

Hard water will not, therefore, form a lather with soap until sufficient has been added to precipitate all the calcium, magnesium and iron in the water as insoluble stearate. For convenience hardness is classified as *temporary* and *permanent.*

(i) **Temporary hardness.**—It is due to the presence of soluble *bicarbonates* of calcium, magnesium and iron in water. Temporary hardness can be removed by : (a) **boiling,** when the soluble bicarbonates are converted into insoluble carbonates which are precipitated, and carbon dioxide is evolved. The method is effective on a domestic scale only.

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2 ;$$
$$Mg(HCO_3)_2 = MgCO_3 + H_2O + CO_2.$$
$$Fe(HCO_3)_2 = FeCO_3 \text{ (ferrous carbonate)} + H_2O + CO_2.$$

Ferrous carbonate is readily oxidised by atmospheric oxygen, and reddish-brown ferric hydroxide is precipitated.

$$4FeCO_3 + 6H_2O + O_2 = 4Fe(OH)_3 + 4CO_2.$$

Magnesium bicarbonate hardness is not fully removed by boiling as magnesium carbonate is to some extent (0.84 gm. per litre) soluble in water.

(b) **Clark's process.**—Temporarily hard water is *softened* for industrial purposes by adding the *calculated* quantity of slaked lime which precipitates the insoluble carbonates.

The mixing of lime and water is done in large settling tanks. After the precipitate has settled down the clear soft water is pumped to reservoirs for distribution ; the water may also be clarified by filtration through beds of coke or sand or a filter press. Only the correct amount of lime is to be added ; addition of more than the requisite quantity makes the water hard again, as the excess lime goes into solution.

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$
$$Mg(HCO_3)_2 + Ca(OH)_2 = MgCO_3 + CaCO_3 + 2H_2O.$$

The magnesium carbonate which is appreciably soluble, then reacts with further quantity of lime to form the insoluble magnesium hydroxide : $MgCO_3 + Ca(OH)_2 = Mg(OH)_2 + CaCO_3$.

(ii) **Permanent hardness.**—This is caused by the presence of the chlorides and sulphates of calcium and magnesium in the water. Like the temporary hardness, permanent hardness can not be removed by mere boiling, or by adding lime, since such methods do not precipitate the calcium or magnesium.

Permanently hard water is softened by the addition of sodium carbonate to water, when insoluble calcium and magnesium carbonates precipitate. The sludge of the insoluble carbonates is removed by filtartion through a filter press.

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4\ ;$$
$$MgCl_2 + Na_2CO_3 = MgCO_3 + 2NaCl.$$

Waters containing dissolved calcium bicarbonate, while falling in drops from the roofs of caves, lose carbon dioxide and deposit columns of calcium carbonate suspending downwards from the roof, known as *stalactites*. The drops falling on the floor deposit columns of calcium carbonate, known as *stalagmites*, which grow upwards to meet the stalactites. These columns are sometimes very beautiful to look at (fig. 71).

Fig. 71

Water softening.—(a) **Lime-soda process.**—Temporary hardness is removed by Clark's process. In softening hard waters for industrial purposes (for use in boilers and laundries) both the *temporary* and *permanent hardnesses* are removed simultaneously by adding *lime and washing soda* in correct proportion, and sometimes also a little caustic soda.

$$Ca(HCO_3)_2 + 2NaOH = CaCO_3 + Na_2CO_3 + 2H_2O.$$

The lime and sodium carbonate precipitate the calcium and magnesium by reactions as stated above.

Magnesium chloride, if present, reacts with lime as follows :

$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2 + CaCl_2.$$

The calcium chloride formed is then precipitated by sodium carbonate. $CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$.

The precipitate is allowed to settle and then removed by filtration.

Crude caustic soda which contains some Na_2CO_3, besides NaOH, may be used with advantage.

(b) **The base exchange or permutit process.**—This is the modern and the most effective method of removing both temporary and permanent hardnesses of water. The permutit is the trade name for artificially prepared sodium aluminium silicate allied to the natural mineral *zeolite*—the permutit is precipitated as a *porous* gel by mixing solutions of sodium silicate and sodium aluminate.

The base exchange material permutit may be formulated as Na_2Ze, where Ze is the zeolite radical.

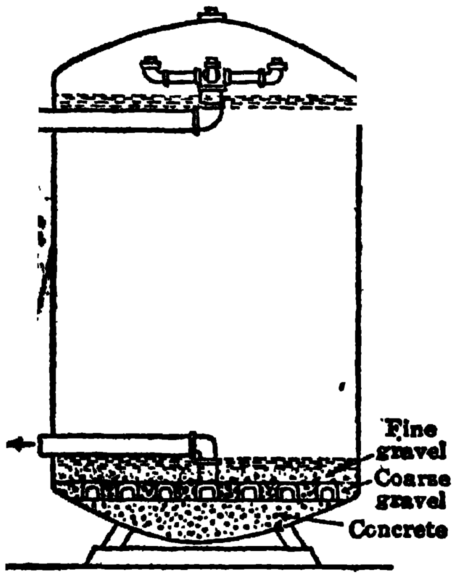


Fig. 72

In the permutit process the hard water is allowed to percolate through a bed of granules of permutit (fig. 72) ; when the calcium and magnesium salts in the water react with the permutit, forming insoluble calcium and magnesium aluminium silicates which are retained in the filter bed. The issuing water, free from calcium and magnesium, is soft.

$$Na_2Ze + Ca(HCO_3)_2 = CaZe + 2NaHCO_3$$
$$Na_2Ze + MgSO_4 = MgZe + Na_2SO_4.$$

The calcium and magnesium ions in the hard water are thus exchanged for an equivalent of sodium ions in the permutit and the hard water gets softened.

After use for some time when the permutit gets exhausted and loses its activity, it is regenerated by percolating with a 10 per cent solution of common salt—the sodium chloride displaces the calcium and magnesium from the exhausted permutit and replaces these by sodium, so that the bed is regenerated and ready for use again :

$$CaZe + 2NaCl \rightleftharpoons CaCl_2 + Na_2Z.$$

Permutit water-softening plants are used in private houses and factories and also for softening public water supplies of towns.

Various synthetic ion-exchange resins are nowadays available for softening water.

(c) **Calgon process.**—Hardwaters may also be softened by adding sodium hexameta-phosphate $(NaPO_3)_6$ technically used under the name *calgon*. The calcium is not precipitated but forms a complex salt with the softening agent which remains in solution and forms no precipitate with soap. Hence its use in laundries for softening water.

Calgon which is formulated as $Na_2[Na_4(PO_3)_6]$ removes the calcium-hardness forming the soluble complex salt $Na_2[Na_2Ca(PO_3)_6]$.

$$Na_2[Na_4(PO_3)_6] + CaSO_4 = Na_2\,[Na_2Ca(PO_3)_6] + Na_2SO_4.$$

It is also used for softening water for boilers, since no scale is deposited and the scales already formed are dissolved.

Water for industrial purposes.—More than 50 per cent of water in chemical industries is used for cooling. Besides, it is used in : (a) **Laundry.**—When hard water is treated with soap, the latter is removed from water as an insoluble precipitate and is not, therefore, available for detergent action until all the calcium and magnesium salts are removed, i.e., until the hard water is softened.

Hard water, therefore, causes waste of soap, when used for laundry purposes, and hence the use of soft water for the same. Laundry water must also be free from iron, as otherwise brown ferric hydroxide would be deposited on fabrics and stain the same.

Estimation of hardness.—The relative hardness of water is expressed in degrees of hardness. 1 degree of hardness is the hardness produced by 1 part of calcium carbonate (or its equivalent) in 100,000 parts of water. Total hardness of water may be estimated by titrating a measured volume of water against a standard soap solution until a lather lasting for 2 minutes is obtained on shaking—the soap solution is previously standardised against water containing a known concentration of calcium chloride. The permutit process gives water of almost zero hardness. The degree of hardness for : soft water 0 to 10° ; medium hard water 10° to 20° ; hard water 20° to 30°, and very hard water above 30°.

(b) **Boiler waters.**—Waters for raising steam in boilers must be soft and must not contain too much dissolved or suspended matter, so as to avoid the troubles of (i) *scale formation*, (ii) *corrosion*, and (iii) *foaming*. The water must be soft as otherwise a deposit of calcium carbonate and calcium sulphate mainly is formed on the walls of the boiler. The formation of this hard, heat-insulating crust, called **boiler scale,** causes a much greater consumption of fuel, and also a rapid deterioration of the boiler due to overheating. The life of the boiler is thus greatly shortened. Under the stress of continued overheating the boiler may give way and burst due to unequal expansion of the body of the boiler and scale. Too much of dissolved matter in boiler waters causes foaming and frothing.

Magnesium chloride, if present in water, is readily hydrolysed, giving hydrochloric acid, which attacks the body of the boiler which is iron, causing *pitting* and *corrosion*. Pitted zones are the vulnerable points in boilers. The boiler water, therefore, must not contain magnesium chloride, i.e., it must be soft. The sea water can not be used in marine boilers, since it contains magnesium chloride :

$$MgCl_2 + H_2O \leftrightarrows Mg(OH)Cl + HCl.$$

Hard waters also deposit 'scale' or 'fur', similar to boiler scale, in household kettles.

(c) Water for other chemical industries such as paper, artificial silk, dyeing, etc., must also be soft and particularly free from iron—the latter, if present, adheres to the fabric in spots forming "iron mould".

Drinking water.—Water for drinking purposes (*potable water*) should be hygienically safe. It should be free from pathogenic bacteria (*i.e.*, disease-producing germs) such as the germs of cholera, typhoid, epidemic diarrhoea, enteric fever and *Bacillus coli*, etc., and any suspended impurity. It must not contain any copper and lead which are cumulative poisons. Presence of nitrates and ammonia in natural waters generally indicates contamination with sewage and decaying matter ; such water is therefore discarded as unsuitable for drinking. Lastly, drinking water should be refreshing to the taste—salts and carbon dioxide add to the freshness of water.

For a large scale supply, as in cities or towns, water is usually taken from a river or a canal running nearby and is purified by sand filtration. Water is pumped up from the source and run into settling tanks where the suspended impurities deposit by sedimentation. Alum is added during this period which helps quick coagulation and settling of the suspended impurities ; precipitated aluminium hydroxide carries down suspended particles of clay, etc. and also some bacteria :

$$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 = 3CaSO_4 + 2Al(OH)_3 + 6CO_2.$$

The partly clarified water is then discharged upon a bed of sand filter which consists of a bottom layer of graded gravel, a middle layer of coarse sand and a top layer of fine sand. The bed is provided with drains below the gravel layer to carry off the filtered water. The sand filter becomes covered with a slimy layer of clay, algae, etc., which removes the suspended impurities and the pathogenic bacteria.

The filtered water is then subjected to **sterilisation** to kill the germs of diseases, if any.

(i) **Chlorination.**—Chlorination with a mild dose of chlorine either by admitting liquid chlorine from steel cylinders or by adding bleaching powder solution to the water supply, is the common method of sterilisation in our country and elsewhere. Water smells of chlorine if too much of it is added. In the *chloramine process* sterilisation is effected by a mixture of chlorine and ammonia which is more effective than chlorine and which also improves the taste of water. Chlorination of water has greatly cut (by 75 per cent.) the death-rate from typhoid.

(ii) **Ultraviolet rays.**—A short exposure to ultraviolet rays, generated with the help of mercury vapour lamps enclosed in quartz containers, kills the bacteria, without imparting any offensive smell or taste to the water.

(iii) **Ozonised air.**—Sterilisation is effected by bubbling ozonised air through filtered water in a tower. Treatment with ozonised air imparts a disagreeable taste and smell to water which must therefore be exposed to air to render it palatable again.

Aeration also greatly helps purification of drinking water. Water is often sterilised, on a small scale, by treatment with potassium permanganate.

The filtered water is then examined—(a) bacteriologically, and (b) chemically, particularly for the poisonous metals, copper and lead, and ammonia whose presence usually indicate sewage contamination.

On a smaller scale for domestic purpose, water is boiled to destroy the bacteria,—boiling effectively sterilises water and hence the practice of boiling drinking water when cholera and typhoid break out,—and then treated with a little alum to coagulate the suspended matter. The water is next filtered through layers of charcoal and sand, contained in perforated earthenware pots.

For domestic use, water may be filtered through **Pasteur-filters** (fig. 73) which consist of one or more porous cylinders P of unglazed porcelain, shaped like hollow candles—the filters effectively retain slimy mass of bacteria and other impurities.

Water for drinking purposes need not be soft—the presence of bicarbonates in hard water gives a refreshing taste to the water. Drinking water must be hard, if it is conveyed through lead pipes, since soft water in presence of dissolved oxygen dissolves out lead as slightly soluble lead hydroxide.

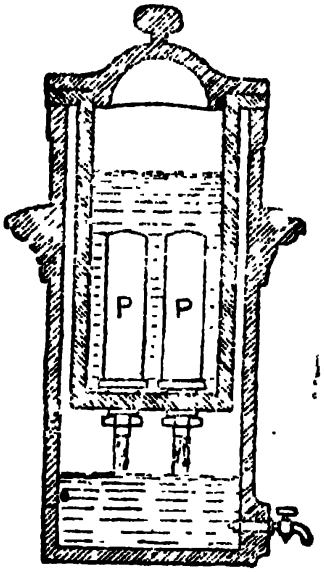
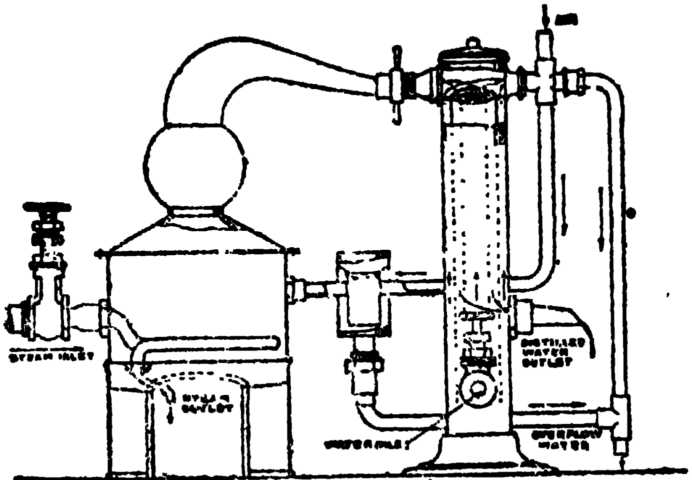


Fig. 73

Pure water.—Natural water usually contains (a) the suspended impurities like fine sand and clay particles, and (b) the dissolved impurities such as salts of sodium, potassium, calcium and magnesium, and the gases such as oxygen, nitrogen, ammonia and carbon-dioxide (page 47). The suspended impurities are removed by *sedimentation and filtration.* Water sufficiently pure for most chemical purposes is purified by *distillation* in a *copper vessel* fitted with a copper or tin condenser. The distilled water, thus prepared, is free from dissolved solids, but still contains the dissolved gases, ammonia and carbon dioxide mainly, and a trace of alkali dissolved from the glass container. Presence of nitrogeneous organic matter in water gives traces of ammonia on distillation. To obtain still purer water, ammonia is first removed by passing chlorine into the boiling distilled water for some time. The chlorine is then boiled out, and the water re-distilled after the addition of a strong solution of potassium permanganate and caustic potash to oxidise the organic impurities, if any, using a tin or a silver condenser. The first and last portions of the distillate are



Distilled Water Plant.

Fig. 74

rejected—only the middle portion is collected in previously *steamed* good Jena or pyrex glasses. This is pure water or what is called **conductivity water.**

For common laboratory use, water is distilled in a copper automatic still (distilled water plant, fig. 74).

Very pure water may be obtained by partially freezing distilled water and collecting the ice—the soluble impurities remaining in unforzen water.

Properties of water.—(i) Pure water is a clear liquid, tasteless and colourless in small quantities but faintly blue when viewed in thickness. The m.p. of ice, 0°C, and the b.p. of water, 100°C, serve as the standard points in thermometry. Pure water is almost a non-conductor of electric current, since it is very slightly ionised into hydrogen and hydroxyl ions : $H_2O \rightleftharpoons H^+ + OH^-$; the conductivity is, however, increased by the addition of electrolytes.

(ii) Water is a stable exothermic compound : $2H_2 + O_2 = 2H_2O$ (steam) $+ 2 \times 58{,}000$ calories. It may be decomposed into its elements at a very high temperature (2000°C or above) by electric sparking or in contact with a white hot platinum. A mixture of hydrogen and oxygen in the ratio of 2 to 1 by volume, obtained by electrolysis, is known as **electrolytic gas.**

Water is decomposed by chlorine in presence of bright sunlight :

$$2H_2O + 2Cl_2 \rightleftharpoons 4HCl + O_2.$$

It may be decomposed by many metals and carbon, and also by electrolysis (p. 10).

(iii) Water readily forms crystals of definite composition, called *hydrates* (p. 53), with many substances, e.g., oxalic acid, $C_2H_2O_4,2H_2O$; blue vitriol, $CuSO_4,5H_2O$—the combined water in these compounds is the water of crystallisation (p. 54).

(iv) Water is a good solvent, particularly for the acids, bases and salts. It dissolves acidic oxides yielding acids, and basic oxides producing hydroxides. Many substances undergo *hydrolysis* (p. 61) with water : $PCl_3 + 3H_2O = H_3PO_3$ (phosphorous acid) $+ 3HCl$.

(v) Trace of moisture is a necessary catalyst in many reactions.

(vi) The usual absorbents for moisture are fused $CaCl_2$, concentrated H_2SO_4, silicagel, P_2O_5 and magnesium perchlorate—of them the last two are the best.

Detection and purity of water.—Water may be detected by its physical properties : freezing point, boiling point and density. Pure water freezes at 0°C and boils at 100°C at 760 mm. pressure. Trace of water is detected by the *blue* colour it gives with *white* anhydrous copper sulphate. A lump of freshly burnt quick lime, on being sprayed with water, crumbles to powder with a hissing noise and evolving much heat.

$$CaO \text{ (quick lime)} + H_2O = Ca(OH)_2 \text{ (slaked lime)}.$$

Pure water leaves no residue on evaporation, so also does not a sample of distilled water—ordinary tap water, however, leaves a solid residue on evaporation. The tests for chloride, sulphate, calcium and ammonia are negative for pure (or distilled) water but are usually positive for tap water, as shown below :

Tests for :	Reagent added	Tap water	Distilled water
(*i*) Chloride	$AgNO_3$ solution + dilute HNO_3	White turbidity	Nil
(*ii*) Sulphate	$BaCl_2$ solution + dilute HCl	White turbidity	Nil
(*iii*) Calcium	Ammonium oxalate solution + dilute acetic acid	White turbidity	Nil
(*iv*) Ammonia	Nessler's reagent	Brown colouration	Nil

Composition of water.—Water was first shown to be a compound of hydrogen and oxygen by Cavendish in 1781. The composition of water can be arrived at both *analytically* and *synthetically*.

Analytical method.—Volumetric composition.—Electrolysis is a ready means of showing that water is made up of two volumes of hydrogen and one volume of oxygen (p. 10).

Synthetic method.—The determination may be carried out by (a) *volumetric* and (b) *gravimetric* methods.

Volumetric Composition.—(i) **Cavendish's experiment.**—Cavendish's experiment (1781) was the first to show that water is formed by igniting a mixture of hydrogen and oxygen in the ratio of 2 to 1 by volume by means of an electric spark. The apparatus he devised was a pear-shaped glass vessel, having two platinum wires sealed at the top for sparking and provided with an air-tight stop-cock at the bottom. The vessel was *exhausted of air*, and then connected to a bell-jar inverted over water and containing a mixture of 2 volumes of hydrogen and one volume of oxygen. Communication was set up between the two vessels by opening up the two stop-cocks, when the gas mixture flowed into the pear and filled it. The stop-cockswere then closed and a spark passed—the gases combined with explosion and moisture was seen inside the pear. This left a vacuum again, and on opening the stop-cocks, some more gas streamed into the pear. The stop-cocks were closed and the gas exploded as before. By repeating the process the whole of the gas mixture was converted into water, and then on opening the stop-cocks *the pear and the bell-jar were completely filled with water.* The experiment, thus showed that water was made up of 2 volume of hydrogen and 1 volume of oxygen (fig. 75). Cavendish's experiment is of historical interest only. Cavendish's experiment was defective in as much as the gas mixture was collected over water.

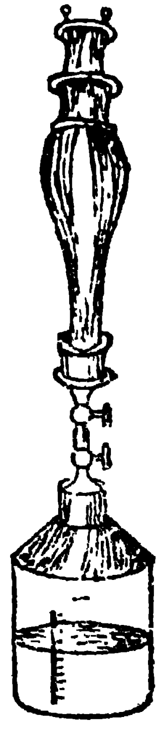


Fig. 75

Cavendish's experiment may be demonstrated in a eudiometer at the closed end of which two platinum wires are sealed for sparking. A certain volume of 2 : 1 hydrogen-oxygen mixture is collected, by the displacement of mercury, in the eudiometer standing over the liquid in a trough. The eudiometer is then held firmly against a rubber pad in the trough, and an electric spark passed. The reaction takes place with explosion, and drops of water appear on the walls of the tube after cooling. On releasing the tube from the

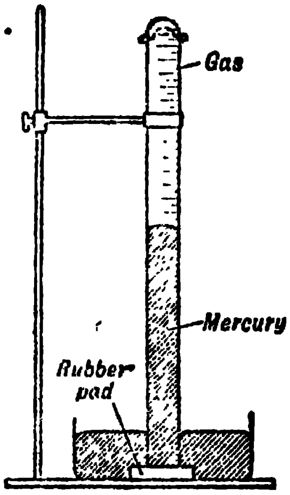


Fig. 76

pressure against the pad, mercury rushes in and completely fills the tube. Hence water is made up of 2 volumes of hydrogen and 1 volume of oxygen. The result confirms that found by electrolysis (fig. 76).

(ii) **Hofmann's experiment.**—The experiment is carried out by sparking a certain volume of 2 : 1 hydrogen-oxygen mixture at a temperature *higher* than the condensing point of steam, 100°C, to obtain the volumetric relation between hydrogen and oxygen and the *steam* produced.

A mixture of 2 volumes of hydrogen and 1 volume of oxygen is introduced into the closed limb of a U-tube (fig. 77), by the displacement of mercury. The closed limb is covered with a wider tube through which passes the vapour of amyl alcohol boiling at 132°C. When he temperature has become steady, the volume of the gas mixture it noted by adjusting to equality the levels of mercury in the two limbs. The open limb is then closed firmly by the thumb and a spark is sent in the gas mixture from an induction coil, by means of platinum wires sealed at the top of the closed limb. There is an immediate contraction on sparking. The levels of mercury are again adjusted to equality after the explosion and the volume noted—it is two-third the original volume of the gas mixture.

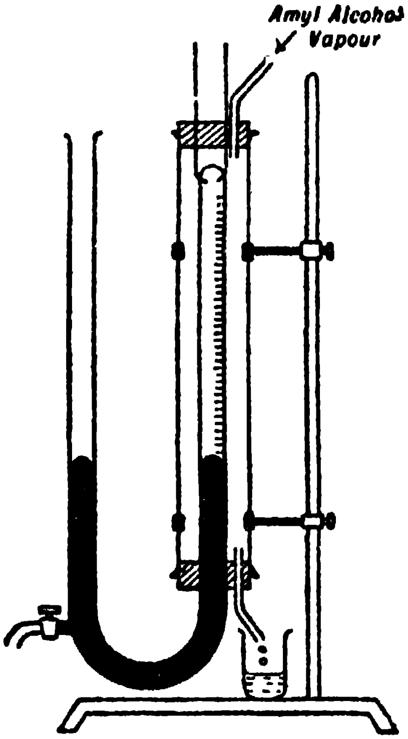


Fig. 77

The vapour of amyl alcohol is then cut off, when the temperature gradually falls below the condensing point of steam, (100°C) ; mercury slowly rises up and finally fills the closed limb completely—two-thirds the volume after explosion is, therefore, occupied by steam.

Formula of steam.—From Hofmann's experiment it follows that :

2 vols. hydrogen + 1 vol oxygen = 2 vols. steam.

By Avogadro's hypothesis, therefore

2 mols. hydrogen + 1 mol. oxygen = 2 mols. steam.

∴ 1 mol. hydrogen H+½ mol. oxygen = 1 mol. steam.

∴ 2 atoms of hydrogen + 1 atom of oxygen = 1 mol. steam, since both hydrogen and oxygen molecules are diatomic.

∴ the molecular formula for steam is H_2O. Now, the vapour density of steam as found by experiment, is 9 and hence its molecular weight 18, which agrees with the formula H_2O for steam.

The experiment only proves that the formula for *steam* is H_2O. Water is an *associated liquid* and contains the molecules, H_2O, $(H_2O)_2$, $(H_2O)_3$ and possibly $(H_2O)_6$.

Gravimetric composition.—Dumas' experiment.—The composition of water by weight was first accurately determined by Dumas in 1842. The method is based upon the formation of water by the reduction of heated copper oxide by means of hydrogen :

$$CuO + H_2 = Cu + H_2O$$

Hydrogen is prepared by the action of zinc upon dilute sulphuric acid in a Woulfe's bottle F, and purified and dried, as described under hydrogen (p. 185). The pure and dry hydrogen is passed over heated copper oxide contained in a vacuous glass bulb, B, (shown on a larger scale above) provided with a long neck—the bulb with the copper oxide being previously weighed. The neck of the copper oxide bulb (fig. 78) is connected with a previously weighed glass bulb, B′, and an absorption system of three previously weighed U-tubes, T_7, T_8 and T_9 ; the first one contained solid caustic potash and the last two phosphorus pentoxide—a guard tube T_{10} of phosphorus pentoxide which is not weighed being attached to the far end of the absorption system to prevent the entry of moisture from the air. The hydrogen is oxidised to water which formed steam—the steam is partially condensed and collected in the bulb, B′, and the vapour absorbed in the three U-tubes T_7, T_8 and

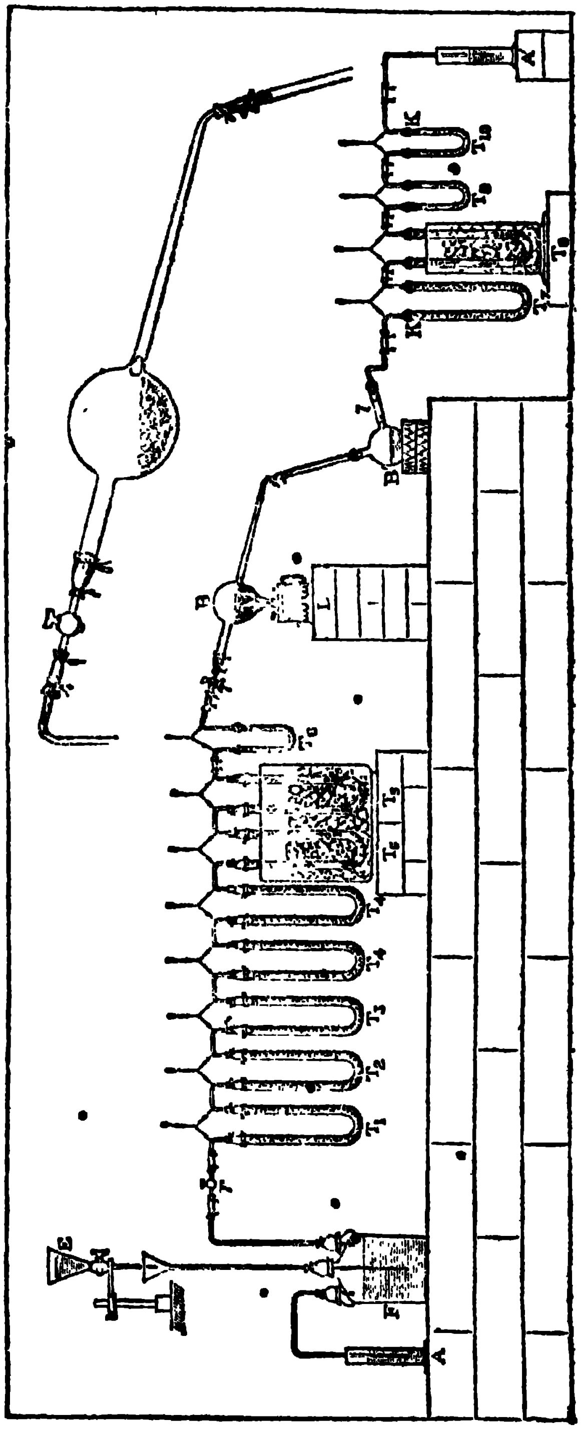


Fig. 78

T_9. The apparatus is cooled in a current of hydrogen after the experiment—the hydrogen is then displaced by air. The bulb B′ and the three U-tubes are weighed again after the experiment—the increase in weight gives the weight of water formed. The copper oxide bulb B is then exhausted and weighed—the decrease in weight gives the weight of oxygen used to produce the water :

From these results the ratio of the combining weights of oxygen and hydrogen is calculated thus :

Loss of weight of copper oxide bulb = weight of oxygen = 0 gm.

Weight of water formed—weight of oxygen = weight of hydrogen = h gm.

∴ the ratio of the combining weights of oxygen and hydrogen = 0/h.

Dumas found the ratio, *oxygen* : hydrogen = 7.89 : 1.

The ratio may be roughly taken to be equal to 8 : 1, then

$$\frac{8}{1}=\frac{a\times\text{atomic weight of oxygen}}{b\times\text{atomic weight of hydrogen}}$$ where a/b is the ratio of the atoms of oxygen and hydrogen in a molecule of water,

$$\therefore\ \frac{8}{1}=\frac{a\times16}{b\times1},\ \text{whence}\ \frac{a}{b}=\frac{1}{2}.$$

∴ the molecular formula of water is H_2O. This is confirmed by determining its vapour density which is found to be 9 : hence the molecular weight 18 which supports the formula H_2O.

Dumas's determination is subject to at least two errors—(i) the sulphuric acid used to prepare hydrogen contained a little *dissolved oxygen* which was reduced to water without producing a corresponding loss of weight of the copper oxide bulb, and (ii) a little *hydrogen* remained occluded in the reduced copper when cooled in the gas.

The most exact experiment on the gravimetric composition of water was carried out by *Morley* who obtained the ratio of oxygen to hydrogen to be equal to 7.9396 to 1. The experiment is described under chemical equivalents (p. 96).

Exercises

1. How would you prepare a specimen of oxygen from potassium chlorate ? What experiments would you perform to demonstrate its principal properties ? How would you show that the residue left after obtaining the oxygen (a) is a chloride and (b) contains potassium and chlorine ?

2. Outline briefly the characteristic properties of various classes of oxides. On what evidence is sodium peroxide classed as a peroxide, carbon dioxide as an acidic oxide, mercuric oxide as a basic oxide ? *Punjab*, 1945

3. How is oxygen obtained on a large scale ? What are its uses ? Mention three compounds which give off oxygen in a fairly pure state when heated, and write equations for their decomposition.

4. Describe how you would prepare in the laboratory as pure a specimen of hydrogen as possible. What is meant by occluded hydrogen ? How would you show (a) that water is formed when hydrogen is burnt in air, and (b) that hydrogen is a reducing agent ? *Calcutta*, 1939

5. Describe methods for the preparation of hydrogen by the action of metals upon (a) cold water, (b) steam, (c) alkali, and (d) a dilute acid. What is meant by nascent hydrogen ? Describe experiments to show that it is a more powerful reducing agent than ordinary hydrogen gas.

6. What are the common impurities which may be present in fresh water taken from natural sources ? How do they affect the suitability of the water for domestic purposes ? Indicate how you would purify it (a) for industrial purposes and (b) for drinking purposes. *Calcutta*, '39

7. What is meant by hardness of water ? What is the hardness due to ? What are the disadvantages of hard water used (a) in the laundry ; (b) in a boiler ? Describe the various methods of the removal of hardness of water.

Bombay, 1947

8. Describe experiments for determining the volumetric composition of steam. How would you therefrom deduce its molecular formula ? *Calcutta*, 1951

9. Write equations to show the action of water upon the following substances—(a) calcium carbide, (b) sodium peroxide, (c) phosphorus pentoxide, (d) sodium, (e) calcium hydride, (f) iron, (g) magnesium, (h) zinc.

10. Outline the methods adopted for the removal of (a) a trace of oxygen from hydrogen, (b) a trace of chlorine from oxygen, (c) a trace of nitrogen from hydrogen, (d) a trace of oxygen from nitrogen, and (e) a trace of moisture from hydrogen.

11. How is ditilled water prepared ? How would you proceed to test its purity ? How can you distinguish it from ordinary drinking water ? Explain why in a chemical laboratory solutions are always made with distilled water.

Calcutta, 1955

12. How and under what conditions does water react with : magnesium, calcium, iron, and carbon ? How would you test if a sample of a liquid is water ?

13. Describe the action of heat on : potassium nitrate, lead nitrate, and sulphuric acid. How you would show that potassium chlorate contains potassium, chlorine and oxygen ? What volume of oxygen at N.T.P. is produced by heating 10 gm. of potassium chlorate ? *Ans.* 2743 c.c.

14. Explain what happens when :

(a) water is added by drops on pellets of sodium peroxide.

(b) a solution of potassium permanganate acidified with dilute sulphuric acid, is gradually added to a solution of hydrogen peroxide.

(c) a paste of bleaching powder is warmed with a few drops of cobalt chloride solution.

(d) a mixture of potassium chlorate and manganese dioxide is heated.

(e) a piece of feebly burning phosphorus put into a jar of oxygen, and its contents then shaken with a few drops of blue litmus solution.

(f) air is shaken with alkaline pyrogallate in a tube.

(g) zinc oxide is heated with a strong solution of caustic soda.

(h) red oxide of mercury is strongly heated in a tube.

(i) a jar of nitric oxide is exposed to air.

(j) a glowing piece of charcoal is introduced into a jar of oxygen, and its contents then shaken with lime water.

15. Explain what happens when :

(a) pellets of sodium are added to a dilute solution of caustic soda.

(b) hydrogen is passed over heated calcium, and the solid product that is formed, is treated with water.

(c) aluminium shavings are boiled with a 20 per cent solution of caustic soda.

(d) a pen-knife is dipped into a solution of ferric chloride containing hydrochloric acid.

(e) tin-foils are boiled with strong hydrochloric acid.

(f) chlorine-water is exposed to sun-light.

What volume of hydrogen at N.T.P. is liberated by treating 1 gram-atom of magnesium with dilute sulphuric acid ? *Ans.* 22.4 litres.

XVIII

OZONE AND HYDROGEN PEROXIDE

Ozone

Ozone is an allotrope of oxygen. Formula O_3. Density 24. Boiling point −112.4°C ; oxygen boils at −183°C. Melting point −249.7°C. 1 volume of water at 0° dissolves 0.49 volume of ozone.

Discovery.—In 1785 Van Marum noticed a peculiar smell near a frictional electrical machine in action, and in 1840 Schonbein attributed this to a new gas, called *ozone* (= I smell).

Formation and Occurrence.—Ozone is formed : (i) by the electric discharges as well as by the action of ultra-violet rays upon oxygen, and hence its presence in the upper layers of the atmosphere ;

(ii) during the electrolysis of acidulated water at low temperature—ozonised oxygen is liberated at the anode ; (iii) during the slow oxidation of white phosphorus and turpentine oil in air ; and (iv) by immersing a hot platinum wire in liquid oxygen. Besides, ozone is formed when fluorine reacts with water at 0°C.

Laboratory preparation.—Mixed with oxygen, ozone is best prepared in the laboratory by the action of **silent electric discharge** upon pure and dry oxygen—oxygen is partially converted into ozone :

$$3O_2 \rightleftharpoons 2O_3 - 68{,}000 \text{ calories.}$$

The change is *endothermic*, and hence the formation of ozone is favoured at high temperature. But since ozone tends to decompose at the ordinary temperature, it must be *rapidly cooled* after its formation at high temperatures. Heat generated by spark discharge would completely decompose ozone, and hence silent discharge is used. Minute sparks of silent discharge is obtained by inserting an insulating material like glass, in the gap through which spark is sent, and the local heat is thereby avoided. *Temperature must be kept low during ozonisation*—indeed any discharge which heats the gas to 200°C is useless for making ozone. By cooling the ozoniser at 0° and avoiding sparks the yield of ozone may be increased—as much as 50% by weight of oxygen may be ozonised.

Two types of ozonisers are usually used, Siemens' and Brodie's :

(a) **Siemens' ozoniser.**—It consists of two coaxial glass tubes—the outside of the outer and the inside of the inner tube being coated with tin foils (fig. 79). A slow current of *pure* and *dry* oxygen is slowly passed through the annular space between the tubes and subjected to *silent electric discharges* by connecting the tin foils to the terminals of an induction coil. Oxygen is partially converted into ozone—the issuing gas turns starch iodide paper blue. The conversion is less than 10 per cent.

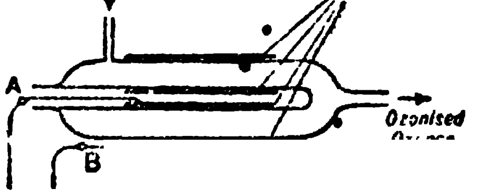


Fig. 79

(d) **Brodie's ozoniser.**—It consists of two concentric glass tubes—the inner tube, closed at the bottom, fitting into the outer by a ground glass joint. The inner tube is filled with dilute sulphuric acid and the outer tube is kept immersed in a jar of dilute sulphuric acid. A slow current of *pure* and *dry* oxygen is passed through the annular space between the two tubes and subjected to silent electric discharges by dipping the copper leads from an induction coil in the sulphuric acid. Oxygen is partially ozonised—the conversion may be as high as 20 per cent (fig. 80).

Ozone may be obtained by electrolysis of ice-cold dilute sulphuric acid with a high current density. Concentration of ozone in the gas liberated at the anode (a thin platinum wire) is about 15 per cent.

Pure ozone.—When ozonised oxygen is passed through a tube cooled in liquid air, it condenses to a deep blue liquid which is a solution of ozone in liquid oxygen. Fractional distillation of this liquid along with the simultaneous pumping off the oxygen yields dark blue *pure liquid ozone*, which on careful evaporation gives deep blue pure gaseous ozone.

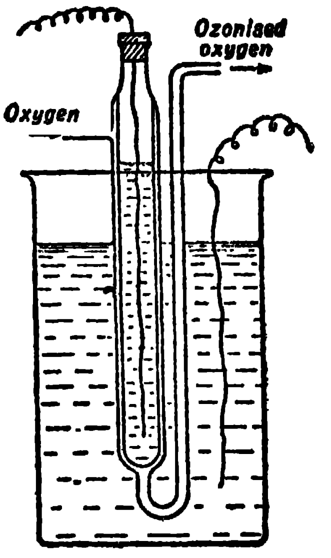


Fig. 80

Industrial Preparation.—Dry air is subjected to the influence of silent high tension electric discharge in Siemens and Halske ozoniser, fig. 81. Each ozone tube consists of a glass or porcelain cylinder surrounding a cylinder of aluminium—six to eight of such tubes are fitted into an iron box through which water flows for cooling purposes. The aluminium cylinder are charged to a potential of 8,000 to 10,000 volts, the glass cylinders being put to earth through the surrounding water and iron box. Dry air enters at the bottom, passes through the ozone tubes and is drawn off from the upper chamber as ozonised air containing about 2 gms. of ozone per cu. m.—with pure oxygen 120—180 gms. are obtained.

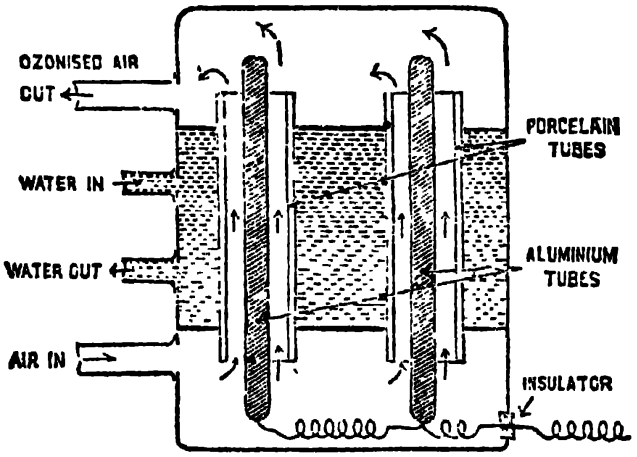


Fig. 81

For a satisfactory yield of ozone—(a) air must be perfectly *dry* and freed from dust particles, (b) temperature must be kept low, and (c) sparking must be rigorously avoided.

Properties.—(i) Ozone is a deep blue gas with a fishy smell ; it may be condensed to a dark blue explosive and highly magnetic liquid.

(ii) Slightly soluble in water (but more soluble than oxygen), 1 volume of water at 0° dissolves 0.49 volume of ozone. Unlike oxygen it dissolves in organic solvents like acetic acid and carbon tetra chloride ; ozone is also *readily soluble in turpentine* oil which is an *absorbent* for the gas. Ozone is heavier than air and oxygen.

(iii) **Stability.**—It slowly decomposes at the ordinary temperature and rapidly at about 300°C into oxygen. The decomposition is catalytically accelerated in presence of dust and organic matter and many finely divided substances, such as platinum black, silver oxide, manganese dioxide and powdered glass : $2O_3 \rightleftharpoons 3O_2$.

(iv) **Oxidising agent.**—Much more active than oxygen, ozone is a powerful oxidising agent, thus : (a) It oxidises lead sulphide to lead sulphate, ferrous salts to ferric salts, nitrites to nitrates, and liberates iodine from acidified potassium iodide solution :

$$PbS+4O_3 = PbSO_4+4O_2 \; ; \quad NaNO_2+O_3 = NaNO_3+O_2.$$

$$2FeSO_4+H_2SO_4+O_3 = Fe_2(SO_4)_3+H_2O+O_2.$$

$$2KI+2HCl+O_3 = 2KCl+I_2+H_2O+O_2.$$

In these reactions only one atom of oxygen in the molecule of ozone is active.

(b) It also oxidises sulphur dioxide to sulphur trioxide, and stannous chloride to stannic chloride, in which the whole of ozone molecule is absorbed ·

$$3SO_2+O_3 = 3SO_3 \; ; \quad 3SnCl_2+6HCl+O_3 = 3SnCl_4+3H_2O.$$

(c) Most metals, except gold and platinum, are oxidised by ozone at ordinary temperature ; *mercury loses its mobility in contact with* **ozone** due to the formation of mercurous oxide :

$$2Hg+O_3 = Hg_2O+O_2.$$

When mercury is shaken in a clean dry flask of ozonised oxygen, the metal adheres to the glass as a mirror. On being shaken with water, the mercury is restored to its original form. Ozone forms a layer of brown oxide on the surface of silver : $2Ag + O_3 = Ag_2O + O_2$ *This reaction may serve as a specific test for ozone.*

(d) Ozone oxidises moist sulphur and phosphorus into sulphuric and phosphoric acids respectively ; moist iodine is converted to iodic acid : $I_2+5O_3+H_2O = 2HIO_3+5O_2$. Ozone liberates halogens from their hydracids : $2HCl+O_3 = Cl_2+H_2O+O_2$.

The liberation of iodine from potassium iodide takes place *in a neutral solution,* which then becomes *alkaline.*

$$O_3+2KI+H_2O = 2KOH+O_2+I_2.$$

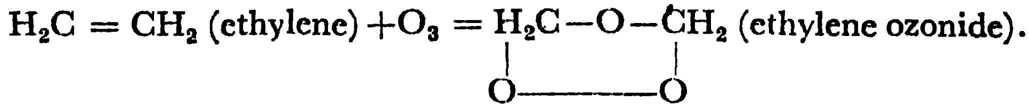
It bleaches vegetable colours by oxidation—indigo is bleached colourless by ozone.

(vi) **Reducing property.**—It behaves as a reducing agent towards hydrogen peroxide, barium peroxide, etc.—but *it is without action upon potassium permanganate or dichromate.*

$$BaO_2+O_3 = BaO+2O_2. \quad H_2O_2+O_3 = H_2O+2O_2.$$

Strictly speaking, it is not a reducing agent, since it is also reduced during the reaction.

(vii) Ozone combines additively with unsaturated organic compounds containing a double bond, e.g., ethylene, turpentine and benzene, to form *ozonides.*



$$H_2C = CH_2 \text{ (ethylene)} + O_3 = \begin{array}{c} H_2C-O-CH_2 \\ |\qquad\qquad | \\ O\text{———}O \end{array} \text{ (ethylene ozonide)}.$$

Ozone rots rubber, since the latter contains unsaturated organic compound.

Tests.—(i) Besides its fishy smell, the action of ozone on mercury is distinctive—even a trace of ozone causes mercury to stick to glass and to become dull in appearance.

(ii) Like other oxidising agents, such as chlorine, nitrogen peroxide, hydrogen peroxide, etc., ozone also liberates iodine from potassium iodide. Consequently, the liberation of iodine from potassium iodide is not specific in the detection of ozone.

Filter papers soaked in alcoholic solutions of tetra methyl base (tetra-methyl-p-p'-diamino-diphenyl methane) and benzidine are coloured as stated below :

Reagent	Ozone	Halogens	Oxides of nitrogen
Tetramethyl base	violet	blue	yellow
Benzidine	brown	blue, then red	blue

These papers are unaffected by hydrogen peroxide.

Absorbent.—Oil of turpentine, and oil of cinnamon.

Uses.—(a) Ozone is a disinfectant, and hence its use in the *sterilisation of water* and the *purification of air* in crowded halls, hospital chambers and underground railways—except at extreme dilutions (some 20 parts per million) ozone, however, attacks mucous membrane and causes headache.

(b) Ozone is used in the *bleaching* of oils, wax, ivory, flour, etc.

(c) For oxidation processes, e.g., potassium manganate to permanganate : $2K_2MnO_4 + H_2O + O_3 = 2KMnO_4 + 2KOH + O_2$, and iso-eugenol to vanilin which is used as a flavouring agent. Sterilisation of water is its most important use—a plant in Paris treats 24,000,000 gallons daily.

Formula of ozone.—Pure and dry oxygen can be made into ozone by silent electric discharge, and the ozone, in its turn, can be converted back into oxygen *only* by heat. *The ozone*, therefore, *is a modification of oxygen only.* Formula for ozone was first determined by Soret in 1866 by the following experiments :

(a) *Equal volumes* of the *same specimen of ozonised* oxygen are taken in two similar flasks (250 c.c. capacity) with long graduated necks dipping under water. Turpentine is admitted into one flask which absorbs the ozone, producing a contraction of, say, x c.c. The other flask is heated until the ozone is completely converted into oxygen, causing an expansion of x/2 c.c. *The contraction on absorption is twice the expansion on heating, that is,*

x c.c. ozone decomposes into x+x/2 c.c. of oxygen.

∴ 1 c.c. of ozone produces $1\frac{1}{2}$ c.c. of oxygen.

By Avogadro's hypothesis, therefore,

1 molecule of ozone produces $1\frac{1}{2}$ molecules of oxygen, i.e., 3 atoms of oxygen. Hence the molecular formula for ozone is O_3.

(b) The formula of ozone was confirmed by Soret by applying Graham's law to the diffusion of ozone from ozonised oxygen. Ozone from ozonised oxygen and chlorine from a mixture of chlorine and oxygen, were each allowed to diffuse into pure oxygen. The relative rate of diffusion of each gas is given by the relation v/V, where v is the volume of gas diffusing in a given time, and V the original volume o the gas in the mixture. v and V were found out as follows : A cylinder (250 c.

capacity) filled with ozonised oxygen is separated from a similar cylinder containing pure oxygen by a plate pierced with a hole (5 m.m. in diameter). Ozone is allowed to diffuse from the first into the second cylinder for a given time (45 minutes). The volume of ozone in each cylinder is then determined by absorption with turpentine —let v_1 and v_2 be the volumes of ozone in the first and second cylinder after the experiment, then relative rate of diffusion of ozone, $v/V = v_2/(v_1 + v_2)$. The volume of ozone may also be calculated from the amount of iodine liberated by potassium iodide by the gas in each cylinder. The experiment was repeated with a mixture of chlorine and oxygen—chlorine was calculased from the amount of iodine liberated from potassium iodide. Relative rases of diffusion were found to be : chlorine 0.227, and ozone 0.271.

By applying Graham's law of diffusion and taking the relative density of chlorine as 35.46 and that of ozone as x,

$$\sqrt{x} : \sqrt{35.46} = 0.227 : 0.271, \text{ and } x = 24.9.$$

Molecular weight of ozone = 2×relative density = 49.8. This corresponds, with the formula O_3.

Vapour density of pure ozone, as determined by Dumas' method, was found to be 24 by Riesenfeld in 1922. This confirms the formula O_3.

Newth's apparatus.—The composition may be conveniently determined by the apparatus devised by Newth (1896). It consists of two concentric glass tubes—fitted into one another by ground glass joint. The space between the two tubes is filled with pure and dry oxygen—its volume being noted by a *sulphuric acid manometer* in communication with the outer tube. A thin glass tube containing turpentine oil is held in the annular space by projections from the inner and outer tubes (fig. 82). The inner tube contains some dilute sulphuric acid. The apparatus is placed in a vessel containing crushed ice and water. Two wires connected with an induction coil dip in this vessel and the inner tube ; on passing a silent electric discharge, oxygen ozonises with a contraction in volume which is read on the manometer. The tube containing turpentine is then broken by rotating the inner tube, when a further contraction due to absorption of ozone takes place. *The contraction on absorption is twice that on ozonisation.*

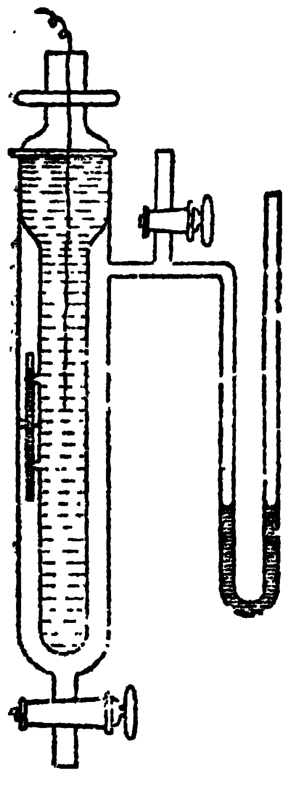


Fig. 82

Let the contraction on ozonisation = x c.c.

the contraction on absorption = $2x$ c.c.

∴ total contraction due to the disappearance of oxygen = $3x$ c.c.

volume of ozone formed = $2x$ c.c.

i.e., 3 vols. of oxygen suffer a contraction of 1 vol. to give 2 vols. of ozone, or in other words,

2 vols. of ozone = 3 vols. oxygen.

By Avogadro's hypothesis, therefore,

2 mols. of ozone = 3 mols. of oxygen,

or 1 mol. of ozone = $1\frac{1}{2}$ mols. of oxygen, i.e., 3 atoms of oxygen.

∴ the formula for ozone is O_3.

Allotropy.—Both oxygen and ozone contain the same element but they differ markedly in their properties. They are called *allotropes*—ozone is the allotropic modification of oxygen.

The property of an element to exist in different forms which differ more or less in their physical properties and to some extent in chemical properties is called allotropy.

Allotropy may be due to difference in the number of atoms in the molecule, as in the case of ozone and oxygen ; it may also be due to the difference in the arrangement of atoms in the molecule—the different allotropes, however, containing the *same* number of atoms in the molecule, as is found in the case of carbon and sulphur. Besides oxygen, carbon and sulphur, the elements nitrogen, phosphorus, silicon, tin, iron, etc. also show allotropy.

Different allotropes differ in their energy content. Rhombic sulphur, for example, is converted into monoclinic sulphur on heating, hence the latter contains more energy than the former.

The same solid substance, elementary or compound, may exist in different crystalline forms. This phenomenon is called **polymorphism.** The existence of red and yellow varieties of mercuric iodide, and the occurrence of silicon dioxide as quartz, sand, etc. are examples of polymorphism. Polymorphism in the case of an element is called allotropy—the term allotropy is, however, applied in the case of an element, be it solid, liquid or gaseous.

Oxidation and Reduction

Oxidation.—The term oxidation is usually used to describe reactions which involve the addition of oxygen to a substance, such as the combustion of carbon into carbon dioxide, the conversion of ferrous oxide into ferric oxide : *the electro-negative element oxygen is the oxidising agent in the above illustration.* $C + O_2 = CO_2$; $4FeO + O_2 = 2Fe_2O_3$. Oxidation has, however, a much wider significance. Since oxygen is a typical electro-negative element, the term oxidation has been extended to include all reactions involving the addition of any electro-negative element or radical, such as sulphur, chlorine, sulphate radical, etc. Thus the conversion of ferrous and cuprous chlorides into ferric chloride and cupric chloride respectively, is regarded as typical oxidation reactions.

$$2FeCl_2+Cl_2 = 2FeCl_3 \; ; \quad 2CuCl+Cl_2 = 2CuCl_2$$

The ratio of the electro-negative or non-metallic to the electro-positive or metallic atoms or groups of a substance is, therefore, increased in oxidation. The removal of hydrogen or the metallic part i.e., the electro-positive atom or radical from a compound also increases the ratio. Therefore :

Oxidation is a reaction which involves (i) the addition or increasing the proportion of oxygen or any electro-negative element or radical to an element or a compound, or, *(ii) the removal or decreasing the proportion of hydrogen or any electro-positive element or radical from a compound.*

Illustrations. (i) **Addition of oxygen.**—Heated in air or oxygen, rose-red copper is converted into black cupric oxide.

$$2Cu+O_2 = 2CuO.$$

Copper is *oxidised to cupric oxide*, since it gains oxygen.

(ii) **Addition of electro-negative element or radical.**—(a) Stannous chloride is oxidised to stannic chloride by the addition of chlorine ; Ferrous chloride is similarly oxidised to ferric chloride by chlorine :

$$SnCl_2+Cl_2 = SnCl_4 ; \quad 2FeCl_2+Cl_2 = 2FeCl_3$$

(b) Acidified solution of ferrous sulphate is oxidised to ferric sulphate by hydrogen peroxide—the sulphate radical is increased in proportion to the iron in the ferric sulphate.

$$2FeSO_4+H_2SO_4+H_2O_2 = Fe_2(SO_4)_3+2H_2O.$$

(iii) **Removal of hydrogen.**—Hydrochloric acid is oxidised to chlorine, when heated with manganese dioxide ; strong sulphuric acid liberates iodine from hydriodic acid ; ammonia can be oxidised to nitrogen by chlorine.

$$4HCl+MnO_2 = MnCl_2+2H_2O+Cl_2,$$
$$2HI+H_2SO_4 = SO_2+2H_2O+I_2.$$
$$2NH_3+3Cl_2 = 6HCl+N_2.$$

(iv) **Removal of electro-positive element.**—Hydrogen peroxide liberates iodine from a solution of potassium iodide—potassium iodide is being oxidised to iodine : $H_2O_2+2KI = 2KOH+I_2$.

Reduction.—Reduction is the exact opposite of oxidation. The ratio of the metallic or electro-positive to the non-metallic or electro-negative atoms or groups of a substance is, therefore, increased in reduction. Therefore :

Reduction is a reaction which involves (i) *the addition or increasing the proportion of hydrogen or any electro-positive element or radical to an element or a compound*, or (ii) *the removal or decreasing the proportion of oxygen or any electro-negative element or radical from a compound.*

Illustrations.—(ii) **Addition of hydrogen.**—Halogens are reduced to their hydracids by hydrogen sulphide and sulphur dioxide. Chlorine, for example, is reduced to hydrochloric acid by the addition of hydrogen, and sulphur precipitates when hydrogen sulphide is passed into chlorine water.

Two acids

$$Cl_2+H_2S = 2HCl+S ; \quad Cl_2+SO_2+2H_2O = 2HCl+H_2SO_4.$$

(ii) **Addition of electro-positive element.**—(a) Cupric chloride is reduced to cuprous chloride by nascent hydrogen or sulphur dioxide :

$$2CuCl_2+2H = Cu_2Cl_2+2HCl.$$
$$2CuCl_2+SO_2+2H_2O = Cu_2Cl_2+H_2SO_4+2HCl.$$

On being heated with mercury, mercuric chloride is reduced to the mercurous chloride : $HgCl_2+Hg = Hg_2Cl_2$.

(b) White insoluble mercurous chloride is precipitated when stannous chloride is added to mercuric chloride solution :

$$2HgCl_2+SnCl_2 = Hg_2Cl_2+SnCl_4.$$

(iii) **Removal of oxygen.**—Hydrogen reduces heated copper oxide to metallic copper : $CuO+H_2 = Cu+H_2O$.

Aluminium powder reduces heated iron oxide to iron by the removal of oxygen : $Fe_2O_3+2Al = 2Fe+Al_2O_3$.

(iv) **Removal of electro-negative element or radical.**—Stannous chloride reduces a hot solution of ferric chloride to the ferrous state. Aluminium chloride is reduced to aluminium by heated sodium.

$2FeCl_3+SnCl_2 = 2FeCl_2+SnCl_4$; $AlCl_3+3Na = Al+3NaCl$.

Ferric chloride (or sulphate) is reduced to the ferrous state by nascent hydrogen :

$FeCl_3+H = FeCl_2+HCl$; $Fe_2(SO_4)_3+2H = 2FeSO_4+H_2SO_4$

The Process of oxidation and reduction always occur simultaneously—whenever one substance is oxidised, another substance must be correspondingly reduced, and *vice versa*. Thus, when carbon monoxide is passed over heated cupric oxide, copper and carbon dioxide are produced—carbon monoxide reduces copper oxide to metallic copper by the removal of oxygen, but is itself oxidised to carbon dioxide by taking up oxygen : $CuO+CO = Cu+CO_2$.

Sulphurous acid is oxidised to sulphuric acid by hydrogen peroxide but the latter itself is reduced to water by loss of oxygen :

$$H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O.$$

Mercuric chloride is reduced to mercurous chloride by stannous chloride but stannous chloride is oxidised to stannic chloride by the addition of chlorine.

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$

An oxidising agent is a substance which brings about the oxidation of another substance and itself gets reduced ; while a **reducing agent** is one which brings about the reduction of another substance but itself gets oxidised.

Examples of a few oxidising agents are :—(a) *ozone* and *oxygen* :

$$2KI + O_3 + H_2O = 2KOH + I_2 + O_2 ;\ 2Mg + O_2 = 2MgO.$$

(b) *Hydrogen peroxide :* $PbS + 4H_2O_2 = PbSO_4 + 4H_2O$.

(c) *Halogens :* $I_2 + H_2O + H_2SO_3 = 2HI + H_2SO_4$. 2 acids

(d) *Potassium permanganate* in acid medium oxidises ferrous salts to the ferric state

$$2KMnO_4 = K_2O + 2MnO + 5{,}O$$
$$K_2O + 2MnO + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O$$
$$10FeSO_4 + 5H_2SO_4 + 5{,}O = 5Fe_2(SO_4)_3 + 5H_2O$$

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

(e) *Potassium dichromate* in acid medium oxidises hydrogen sulphide to sulphur :

$$K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3{,}O$$
$$K_2O + Cr_2O_3 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O$$
$$3H_2S + 3O = 3H_2O + 3S$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

(f) *Sodium peroxide* oxidises chromium hydroxide to yellow sodium chromate :

$$2Cr(OH)_3 + 3Na_2O_2 = 2Na_2CrO_4 + 2NaOH + 2H_2O.$$

SO_2 as an oxidising agent :- $2H_2S + SO_2 = 2H_2O + 3S$

(g) *Concentrated nitric acid* oxidises phosphorus to phosphoric acid :

$$10HNO_3 = 5H_2O + 5NO + 5NO_2 + 10,O$$
$$4P + 10,O = 2P_2O_5$$
$$2P_2O_5 + 6H_2O = 4H_3PO_4$$
$$\overline{4P + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2.}$$

(h) Hot concentrated sulphuric acid oxidises carbon to carbon dioxide :

$$2H_2SO_4 = 2H_2O + 2SO_2 + 2,O$$
$$C + 2,O = CO_2$$
$$\overline{C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O.}$$

(i) *Potassium chlorate* oxidises sulphur dioxide to sulphuric acid :

$$KClO_3 + 3SO_2 + 3H_2O = KCl + 3H_2SO_4$$

Potassium nitrate acts as an oxidising agent in the gunpowder.

(j) *Manganese dioxide* oxidises hydrochloric acide to chlorine :

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

Examples of a few reducing agents are.—

(a) *Hydrogen :* $FeCl_3 + H$ (nascent) $= FeCl_2 + HCl$.

(b) *Hydrogen sulphide :* $2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$.

(c) *Sulphur dioxide :* $2FeCl_3 + 2H_2O + SO_2 = 2FeCl_2 + 2HCl + H_2SO_4$.

(d) *Hydriodic acid :* $2HI + H_2O_2 = 2H_2O + I_2$.

(e) *Stannous chloride :* $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$.

(f) *Carbon* and *carbon monoxide* :

$$PbO + C = Pb + CO \; ; \; Fe_2O_3 + 3CO = 2Fe + 3CO.$$

(g) *Potassium cyanide :* $SnO_2 + 2KCN = Sn + 2KCNO$.

(h) *Metals*, e.g., sodium, magnesium, aluminium, etc :

$$SiO_2 + 2Mg = 2MgO + Si \; ; \; 3SiCl_4 + 4Al = 4AlCl_3 + 3Si.$$

Valency change in oxidation and reduction.—*Oxidation and reduction reactions involve change of valency. The positive valency of an element is increased in the process of oxidation; reduction is the decrease in the positive valency* (*or increase of negative valency*).

Thus, when ferrous chloride is oxidised by chlorine into ferric chloride, the iron is oxidised, since its positive valency has increased from +2 to +3, whilst the oxidising agent chlorine is reduced, since its valency is changed from zero to −1 (chloride ion). *All free elements are taken of zero valency.*

During the reduction of ferric chloride by nascent hydrogen to the ferrous state, the positive valency of iron is decreased from +3 to +2, while the valency of hydrogen is changed from zero to +1 (in hydrochloric acid) and the latter is therefore oxidised :

$$2FeCl_2 + Cl_2 = 2FeCl_3 \; ; \; FeCl_3 + H = FeCl_2 + HCl.$$

Electronic definitions of oxidation and reduction.—When ferrous chloride is oxidised by chlorine in aqueous solution :

$$2FeCl_2 + Cl_2 = 2FeCl_3$$

or expressed ionically, $2Fe^{++} + Cl_2 = 2Fe^{+++} + 2Cl^-$, the ferrous ion Fe^{++} is converted into the ferric ion Fe^{+++} by the *loss of an electron* (oxidation) and the neutral chlorine into negatively charged chloride ion Cl^- by the *gain of an electron* (reduction), that is,

$$Fe^{++} - e = Fe^{+++} \; ; \; Cl + e = Cl^-.$$

Similarly, when ferric chloride is reduced by nascent hydrogen

$FeCl_3 + H = FeCl_2 + HCl$ or expressed ionically,

$Fe^{+++} + H = Fe^{++} + H^{+}$, the ferric ion Fe^{+++} gains an electron to be reduced to the ferrous ion Fe^{++}, whilst the reducing agent hydrogen loses the electron to be oxidised into the hydrogen ion H^{+}, that is,

$$Fe^{+++} + e = Fe^{++} ; \qquad H - e = H^{+}$$

This leads to the view that *oxidation is a process which involves the loss of one or more electrons by atoms or ions, whereas reduction is a process which results in the gain of one or more electrons by atoms or ions.*

An oxidising agent is one that gains electrons and is reduced to a lower valency state, while a reducing agent is one that loses electron and is oxidised to higher valency state. Thus the use of chlorine as an oxidising agent involves its reduction into chloride ion by the addition of electrons, while the use of sodium as a reducing agent is accompanied by its oxidation into sodium ion by loss of electrons :

$$Cl_2 + 2e = 2Cl^{-} ; \quad Na - e = Na^{+}$$

In oxidation-reduction processes (or *redox processes*) electrons are transferred from the reducing agent to the oxidising agent.

Few experiments to illustrate processes of oxidation and reduction.—

(1) Stannous chloride solution is added by drops to a *hot yellow* solution of ferric chloride until just colourless—the ferric chloride is reduced to the ferrous state :

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

(2) Stannous chloride solution is added gradually to a solution of mercuric chloride, when a white precipitate of mercurous chloride first forms, which finally turns grey due to its reduction to metallic mercury :

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4 ; \; Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

(3) Potassium iodide solution is added to a solution of copper sulphate—a white precipitate of cuprous iodide is formed, which is coloured brown by iodine that is set free in the reaction : $2CuSO_4 + 4KI = 2K_2SO_4 + Cu_2I_2 + I_2$.

Cupric copper (valency 2) has been reduced to the cpurous state (valency 1).

(4) Sulphur dioxide is bubbled through a green solution of cupric chloride solution when cuprous chloride is obtained as a *white* precipitate ; cupric chloride has been reduced to the cuprous state by sulphur dioxide :

$$2CuCl_2 + H_2SO_3 + H_2O = Cu_2Cl_2 + H_2SO_4 + 2HCl.$$

(5) A filter paper soaked in lead acetate solution is exposed to the action of hydrogen sulphide gas, when it turns *black* due to the formation of lead sulphide ; the filter paper is again bleached *white* when dipped into a solution of hydrogen peroxide in a basin. $PbS + 4H_2O_2 = PbSO_4 + 4H_2O$.

The lead sulphide is oxidised to lead sulphate which is white in colour.

(6) Potassium iodide is heated with strong sulphuric acid in a test tube, when *violet* vapours of iodine are evolved :

$$2KI + 2H_2SO_4 = 2KHSO_4 + 2HI ; \; 2HI + H_2SO_4 = 2H_2O + SO_2 + I_2.$$

(7) A piece of glowing charcoal is inserted in strong nitric acid in which it burns brilliantly—the carbon is oxidised to carbon dioxide by the nitric acid :

$$C + 4HNO_3 = CO_2 + 4NO_2 + 2H_2O.$$

(8) Hydrogen sulphide gas is passed into strong nitric acid when sulphur deposits as a white precipitate, and brown fumes of nitrogen peroxide are evolved : The sulphur is also partially oxidised to sulphuric acid.

$$2HNO_3 + H_2S = 2H_2O + 2NO_2 + S \; ; \; S + 6HNO_3 = H_2SO_4 + 6NO_2 + 2H_2O.$$

The sulphur is filtered off ; the filtrate gives a white precipitate of barium sulphate, insoluble in hydrochloric acid, with barium chloride solution ; hence the formation of sulphuric acid is confirmed : $BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$.

Catalytic oxidation and reduction.—These processes are technically important, *e.g.*, catalytic oxidation of (a) ammonia to nitric acid in Ostwald process, (b) sulphur dioxide to sulphuric acid in contact process, and catalytic reduction of acetylene to ethylene in presence of nickel catalyst :

$$HC \equiv CH \text{ (acetylene)} + H_2 = H_2C = CH_2 \text{ (ethylene)}.$$

✓ Hydrogen Peroxide

Hydrogen peroxide was discovered by Thenard in 1818. It is formed in traces during the combustion of hydrogen in oxygen—hydrogen flame directed on to ice produces water containing a little hydrogen peroxide.

Hydrogen peroxide is prepared by the action of cold dilute mineral acids such as dilute sulphuric acid, upon a suitable metallic peroxide, such as barium peroxide, sodium peroxide, etc.

Laboratory preparation :—(a) **From barium peroxide** : Finely ground barium peroxide is made into a paste of *hydrated* barium peroxide, $BaO_2, 8H_2O$, by treatment with water—anhydrous barium peroxide is not readilv acted on by dilute sulphuric acid since the particles become coated wihh insoluble barium sulphate.

The paste is gradually added to *cold dilute* sulphuric acid (1 vol. of acid to 5 vols. of water) in a beaker cooled in crushed ice, stirring the mixture with a glass rod, until the solution is *just faintly acidic* —a trace of acid stabilises hydrogen peroxide. Barium peroxide reacts with sulphuric acid, forming hydrogen peroxide and a white precipitate of barium sulphate. The barium sulphate is allowed to settle and then filtered off—the filtrate is an aqueous solution of 10 to 20% hydrogen peroxide. $BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$.

By passing carbon dioxide into a suspension of barium peroxide in water, barium carbonate is precipitated and a solution of hydrogen peroxide is formed—the barium carbonate is filtered off :

$$BaO_2 + H_2O + CO_2 = BaCO_3 + H_2O_2.$$

(b) **From sodium peroxide.**—Calculated amount of sodium peroxide is slowly added to a solution of sodium dihydrogen phosphate, cooled in ice, until the solution is *just acidic* :

$$Na_2O_2 + 2NaH_2PO_4 = 2Na_2HPO_4 + H_2O_2.$$

Most of the disodium hydrogen phosphate separate on cooling as the hydrate, $Na_2HPO_4, 12H_2O$ and is filtered off, leaving a strong solution of hydrogen peroxide.

Commercial preparation.—(a) **From barium peroxide.**—Barium peroxide is hydrated by treatment with steam and the paste of hydrated barium peroxide is decomposed by cold dilute sulphuric acid, as in the laboratory process. But more recently it is decomposed by phosphoric acid.

$$3BaO_2 + 2H_3PO_4 = Ba_3(PO_4)_2 + 3H_2O_2.$$

The precipitated barium phosphate is filtered off, leaving a solution of hydrogen peroxide which is concentrated by distillation under reduced pressure.

The barium phosphate is decomposed by dilute sulphuric acid to liberate the phosphoric acid to be used again : $Ba_3(PO_4)_2 + 3H_2SO_4 = 3BaSO_4 + 2H_3PO_4$.

The product obtained by this method is of better stability, since phosphoric acid acts as a preservative of hydrogen peroxide. The barium sulphate precipitate is used as a pigment extender under the name of **blanc fixe.**

(b) **From sodium peroxide.—Merck's process :** Calculated quantity of sodium peroxide is slowly added to ice-cold, dilute (20 per cent) sulphuric acid solution :

$$Na_2O_2 + H_2SO_4 = H_2O_2 + Na_2SO_4.$$

Most of the sodium sulphate separates on cooling as Glauber's salt, Na_2SO_4, $10H_2O$, and is filtered off. The filtrate, on distilling in vacuo, yields 30% solution of hydrogen peroxide, known as Merck's **perhydrol.**

(c) **From perdisulphuric acid.**—Hydrogen peroxide is obtained by electrolytic methods which involve the intermediate formation of perdisulphuric acid or its salts. Persulphuric acid is obtained by the electrolysis of ice-cold, 50 per cent sulphuric acid, using a platinum anode and a high current density ; this is hydrolysed with dilute sulphuric acid and the resulting hydrogen peroxide is distilled under reduced pressure. The hydrogen peroxide is obtained in pure 30 per cent solution.

Sulphuric acid at this concentration is ionised to H^+ and HSO_4' (bisulphate) ions : $HO-SO_2-OH \rightleftharpoons H^+ + (O-SO_2-OH)^-$.

Hydrogen is liberated at cathode : $2H^+ + 2e = H_2$.

At anode HSO_4' ions are discharged and condense to yield perdisulphuric acid, $H_2S_2O_8$, thus :

$$\begin{array}{lcl} [O-SO_2-OH]^- & \qquad & \begin{array}{l} O-SO_2-OH \\ | \\ O-SO_2-OH \end{array} \quad + 2e \\ [O-SO_2-OH]^- & & \end{array}$$

Hydrolysis of $H_2S_2O_8$ is effected as follows :

$$\begin{array}{c} HO-SO_2-O-O-SO_2-OH \\ HO-H + H-OH \\ = HO-SO_2-OH + H_2O_2 + HO-SO_2-OH. \end{array}$$

In another process ammonium bisulphate $(NH_4)HSO_4$ is electrolysed and the resulting solution of ammonium persulphate $(NH_4)_2S_2O_8$, is hydrolysed and distilled under reduced pressure to give hydrogen peroxide.

$$(NH_4)_2S_2O_8 + 2H_2O = 2(NH_4)HSO_4 + H_2O_2$$

The solution of hydrogen peroxide, made by electrolytic method, may be concentrated by distillation under low pressure upto about 90 per cent H_2O_2 which is *fairly stable*—the process developed in Germany during last Great War for rocket propulsion. Pure hydrogen peroxide is fairly stable in absence of sun-light.

Pure Hydrogen peroxide.—The dilute aqueous solution of hydrogen peroxide is concentrated : (i) by evaporation in an open dish on a water bath, when the more volatile water vaporises away (b. p. of water 100°C ; that of hydrogen peroxide 151°C). The process is continued until the solution contains about 60 per cent hydrogen peroxide—further evaporation merely decomposes it into water and oxygen. (ii) by distillation under reduced pressure—the concentrated solution, on successive distillations under reduced pressure of 15 mm., yields hydrogen peroxide of 99 per cent purity (fig. 83).

Crystals of pure hydrogen peroxide separate if the 99 per cent solution of hydrogen peroxide, cooled to—10°C, be seeded with a crystal of hydrogen peroxide, which is first obtained by cooling portion of the 99 per cent solution with solid carbon dioxide and ether.

Properties.—(i) Pure hydrogen peroxide is a colourless (in small amounts, but blue in bulk), syrupy liquid with the smell like that of nitric acid. It is soluble in water and ether. Its specific gravity is 1.46 at 0°. It freezes at—0.89°C. It decomposes explosively at its boiling point 151°C but may be distilled under reduced pressure —it boils at 84°C under a pressure of 68 m.m.

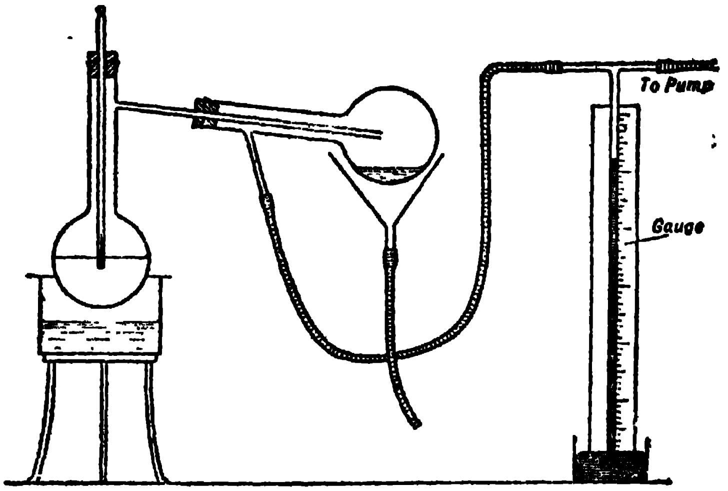


Fig. 83

Hydrogen peroxide yields *addition compounds* with some salts, e.g., $(NH_4)_2SO_4,H_2O_2$, and with urea, $CO(NH_2)_2,H_2O_2$—the hydrogen peroxide behaving like water of crystallisation. The addition compound with urea stablised by citric acid, is known as *hyperol.*

(ii) **Stability.**—It slowly decomposes at the ordinary temperature, and readily when heated, forming water and oxygen and evolving much heat. $2H_2O_2 = 2H_2O + O_2 + 46{,}120$ calories.

The decomposition is promoted by many catalysts such as finely divided metals like gold and platinum black and certain solids such as manganese dioxide and the enzyme *catalase* which is present in milk and blood. The decomposition is also caused by *traces of alkali.* But small quantities of acid, namely, phosphoric acid, calcium chloride, glycerine, etc. retard the decomposition, i.e., they act as negative catalysts, and are, therefore, used as preservatives for commercial hydrogen peroxide.

Colloidal platinum brings about a quick catalytic decomposition of hydrogen peroxide, yielding oxygen.

(iii) **Oxidising agent.**—It is a powerful oxidising agent ; thus :

(a) It liberates iodine from acidified potassium iodide—a reaction used for the estimation of hydrogen peroxide :

$$2KI + H_2O_2 + 2HCl = 2KCl + I_2 + 2H_2O.$$

(b) Lead sulphide is oxidised to lead sulphate :

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O.$$

The conversion of black lead sulphide into white lead sulphate is employed in restoring the colour of old oil-paintings which is tarnished due to the action of atmospheric hydrogen sulphide upon 'white lead' paints ; hence the use of hydrogen peroxide as a bleaching agent.

(c) Ferrous salts are oxidised to ferric salts in acid solutions :

$$2FeSO_4 + H_2SO_4 + H_2O_2 = Fe_2(SO_4)_3 + 2H_2O.$$

(d) It oxidises sulphurous acid to sulphuric acid, arsenious acid to arsenic acid, and hydrogen sulphide to sulphur and water :

$$H_3AsO_3 \text{ (arsenious acid)} + H_2O_2 = H_3AsO_4 \text{ (arsenic acid)} + H_2O.$$

$$H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O \; ; \; H_2S + H_2O_2 = 2H_2O + S.$$

(e) Hydrogen peroxide *oxidises* potassium ferrocyanide to potassium ferricyanide in *acid solution* :

$$2K_4Fe(CN)_6 + H_2O_2 + 2HCl = 2K_3Fe(CN)_6 + 2KCl + 2H_2O.$$

An *alkaline* solution of potassium ferricyanide is *reduced* to potassium ferrocyanide by hydrogen peroxide :

$$2K_3Fe(CN)_6 + 2KOH + H_2O_2 = 2K_4Fe(CN)_6 + 2H_2O + O_2.$$

(iv) **Reducing property.**—It behaves as a reducing agent towards powerful oxidising agents.

(a) Potassium permanganate (*pink in colour*) in acid solution is rapdily reduced to a colourless solution :

$$2KMnO_4+3H_2SO_4+5H_2O_2 = K_2SO_4+2MnSO_4+8H_2O+5O_2.$$

(b) Silver oxide is reduced to metallic silver ; ozone is reduced to oxygen. Solutions of bleaching powder and sodium hypobromite liberate oxygen.

$$Ag_2O+H_2O_2 = 2Ag+H_2O+O_2 \; ; \; O_3+H_2O_2 = H_2O+2O_2.$$

$$NaOBr \text{ (sodium hypobromite)} + H_2O_2 = NaBr+H_2O+O_2.$$

(v) **Acid properties.**—Pure hydrogen peroxide has *feeble acidic properties*. It turns blue litmus red and reacts with barium hydroxide to give a precipitate of barium peroxide ; with sodium carbonate solution it yields carbon dioxide—oxygen is, however, evolved by the catalytic decomposition of H_2O_2, if the carbonate be in excess.

$$Ba(OH)_2 + H_2O_2 = BaO_2 + 2H_2O \; ;$$

$$Na_2CO_3 + H_2O_2 = Na_2O_2 + H_2O + CO_2$$

Tests for hydrogen peroxide.—(i) Hydrogen peroxide liberates iodine from potassium iodide solution, which gives a blue colour with starch ; ozone also gives this reaction. But hydrogen peroxide *alone* readily liberates iodine potassium iodide *in presence of ferrous sulphate*.

(ii) A solution of potassium chromate acidified with dilute sulphuric acid is added to a dilute solution of hydrogen peroxide in a separating funnel. The solution is rapidly shaken with ether, which floats on the surface with a *deep blue colour*. This is the delicate '**perchromic acid' test** for hydrogen peroxide, and is due to the formation of chromium peroxide, CrO_5, which is soluble in ether.

$$H_2CrO_4 + 2H_2O_2 = CrO_5 + 3H_2O.$$

(iii) Hydrogen peroxide is added to a *pink* solution of potassium permanganate acidified with dilute sulphuric acid—the pink colour is readily discharged, yielding a colourless solution.

(iv) Hydrogen peroxide is added to a solution of titanium dioxide in dilute sulphuric acid, an *orange yellow colour* develops due to the formation of titanium peroxide. $TiO_2 + H_2O_2 = TiO_3 + H_2O$ (titanium peroxide). The test is highly delicate.

The reagent is prepared by heating titanium dioxide TiO_2, with concentrated sulphuric acid, cooling and diluting with water.

Uses of Hydrogen Peroxide.—(i) As an oxidising agent in the laboratories; Hydrogen peroxide in presence of ferrous sulphate (Fenton's reagent) is often used as an oxidising agent.

(ii) For restoring the colour of old oilpaintings containing white lead.

(iii) For bleaching the delicate fabrics like wool, silk, feather, ivory, etc., which would be injured by chlorine. Hydrogen peroxide bleaches hair to golden yellow colour.

(iv) As an antiseptic wash in surgery in dressing wounds. It is largely used as a gargle, spray and mouth-wash.

(v) As an *antichlor* to remove excess of chlorine from bleached fabrics :

$$H_2O_2 + Cl_2 = 2HCl + O_2.$$

(vi) 85 per cent solution of hydrogen peroxide had been used in Germany during the last war in the propelling charge of V-2 jet-propelled bombs—the hydrogen peroxide reacts with permanganates to give steam and oxygen for rocket propulsion. The concentrated hydrogen peroxide has also been used in burning fuels such as petrol, alcohol and hydrazine hydrate in producing power.

Strength of hydrogen peroxide solution.—It is stated in terms of volume of oxygen evolved on heating hydrogen peroxide solution. This is usually expressed in '**volume strength**,' which means the c.c.'s of oxygen at N.T.P. that can be obtained from 1 c.c. of a sample of a solution of hydrogen peroxide.

$$\begin{array}{lcl} 2H_2O_2 & = & 2H_2O + O_2 \\ 68 & & 22400 \text{ c.c. of oxygen at N.T.P.} \end{array}$$

∴ 1 gm. of hydrogen peroxide gives 329.4 c.c. of O_2 at N.T.P.

Or 100 c.c. of 1 per cent solution gives 329.4 c.c. of O_2 at N.T.P.

∴ 1 c.c. of 1% solution of H_2O_2 gives 3.294 c.c. of O_2 at N.T.P.

1% solution of hydrogen peroxide, therefore, is of '3.294 volume' strength.

10 volume hydrogen peroxide is of 3.04 per cent strength ; 100 volume hydrogen peroxide is of 30 per cent strength.

A sample of hydrogen peroxide of 'v volume' strength is v/3.294 per cent solution.

Formula of hydrogen peroxide.—Hydrogen peroxide contains hydrogen and oxygen only. Thenard heated a weighed quantity of hydrogen peroxide, and determined the weight of oxygen that is liberated. 34 parts by weight of hydrogen peroxide were found to yield 16 parts by weight of oxygen and 18 parts of water. But 18 parts of water contain 2 parts of hydrogen and 16 parts of oxygen by weight. 34 parts of hydrogen peroxide, therefore, contain 2 parts of hydrogen and 32 parts of oxygen by weight. Consequently, the atomic ratio of hydrogen to oxygen in hydrogen peroxide is $\frac{2}{1} : \frac{32}{16}$ i.e., 1 : 1, and hence its simple formula is (HO)n.

The vapour density of hydrogen peroxide as determined under reduced pressure is 17 ; the molecular weight is, therefore, 34.

$$\therefore \quad (HO)n = 34, \text{ or } (1+16)n = 34, \quad \therefore \quad n = 2,$$

The formula for hydrogen peroxide is, therefore, H_2O_2.

Its structural formula is : $H - O - O - H$.

Distinctive tests of ozone and hydrogen peroxide.—

Reagents	Ozone	Hydrogen peroxide
(i) Potassium iodide solution	Liberates iodine	Liberates iodine
(ii) KI solution + $FeSO_4$ solution	Does not liberate iodine	Liberates iodine
(iii) K_2CrO_4 solution + dilute H_2SO_4 + ether	No reaction	Deep blue ether layer
(iv) $KMnO_4$ solution + dilute H_2SO_4	No reaction	Pink colour is discharged
(v) Titanium dioxide + dilute H_2SO_4	No reaction	Orange yellow colour
(vi) Test paper soaked in alcoholic solution of :		
(a) benzidine	Turns brown	No change
(b) tetramethyl base	Turns violet	No change
(vii) (a) Mercury	Mercury loses mobility	No change
(b) Warm silver	Silver blackens	No change

Comparison of ozone and hydrogen peroxide.—

Property	Ozone	Hydrogen peroxide
(i) Nature, colour, odour, etc.	Allotrope of O_2 ; endothermic substance. Deep blue gas ; fishy smell.	A peroxide ; exothermic compound. Clear syrupy liquid ; smells like nitric acid.
(ii) Reaction to litmus	Neutral.	Acidic ; pure H_2O_2 turns blue litmus red.
(iii) Solubility in : (a) water, (b) organic solvents	Slightly soluble. Soluble in CCl_4 (deep blue solution). Soluble in turpentine (absorbent for O_3).	Freely soluble. Freely soluble in ether.
(iv) Stability	Unstable ; slowly breaks up evolving O_2—decomposition is accelerated by heat and by contact with rough surfaces of dust, platinum black, etc. $2O_3 \leftrightarrows 3O_2$;	$2H_2O_2 = 2H_2O + O_2$
(v) Oxidising property	Powerful oxidising agent. Liberates iodine from KI.	Powerful oxidising agent. Liberates iodine from KI.
(vi) Reducing property	Reacts with many oxidising agents : $H_2O_2 + O_3 = H_2O + 2O_2$.	Reacts with many oxidising agents : $Ag_2O + H_2O_2 = 2Ag + H_2O + O_2$
(vii) Bleaching property	Bleaches indigo by oxidation.	Bleaches wool, silk, etc. by oxidation.
(viii) Addition compounds	Forms ethylene ozonide.	Froms addition compounds, e.g., hyperol.
(ix) Distinctive tests	*Vide supra.*	*Vide supra.*

Exercises

1. Describe how oxygen can be ozonised, and illustrate with reference to three examples how ozonised oxygen differs from ordinary oxygen. How may the formula of ozone be established ? *Punjab* '51

2. Explain what is meant by the term allotropy. How is ozone prepared, and what are its principal properties ? How does ozone react (a) with lead sulphide, (b) with mercury, (c) with potassium iodide, (d) when passed through a heated tube ? Give three distinctive tests for ozone. How would you show that the substance is a modification of oxygen only ? *Calcutta* 1954

3. Describe the preparation of hydrogen peroxide. What are its distinctive tests and uses ? Compare the properties of ozone and hydrogen peroxide. How does hydrogen peroxide react with (i) acidified potassium iodide, (ii) lead sulphide, (iii) silver oxide, (iv) ozone, and (v) acidified potassium permanganate, (vi) hydrochloric acid ? *Calcutta* '53

4. How can you convert (a) ferric chloride into ferrous chloride, (b) stannous chloride into stannic chloride, (c) mercurous nitrate into mercuric nitrate, and (d) cupric chloride into cuprous chloride ?

Express the changes by equations and justify the statement that these reactions involve an oxidising or a reducing process. *Calcutta* '45.

5. Explain the meaning of the terms 'oxidation' and 'reduction' in chemical reactions. Discuss why a process of oxidation is always attended by that of reduction and *vice versa*. Illustrate your answer with reference to the following reactions between —(i) zinc and dilute sulphuric acid, (ii) potassium iodide and copper sulphate solution, and (iii) iodine and a solution of hydrogen sulphide. *Cambridge Scholarship.*

6. Explain what happens when :

(i) hydrogen peroxide solution is shaken with platinum black ;
(ii) hydrogen peroxide is added to an alkaline solution of potassium ferricyanide ;
(iii) ozone is passed through a red hot glass tube ;
(iv) hydrogen peroxide solution is shaken with manganese dioxide ;
(v) ozonised oxygen is led into a solution of hydrogen peroxide ;
(vi) ozone is led into a solution of ethylene ;
(vii) ozonised oxygen is bubbled through a solution of potassium iodide ;
(viii) a lead acetate paper is exposed to the action of hydrogen sulphide, and then steeped into hydrogen peroxide solution ;
(ix) a solution of ferrous sulphate containing a little dilute sulphuric acid is treated with hydrogen peroxide ;
(x) ozone is passed into a solution of stannous chloride containing hydrochloric acid ;
(xi) ozonised oxygen is bubbled through a strong solution of hydrochloric acid, and the solution is then tested with a starch-iodide paper ;
(xii) carbon dioxide is passed into a suspension of barium peroxide in water.

7. Explain clearly the terms oxidation and reduction. Illustrate your answer with experiments involving the use of : chlorine, hydrogen sulphide, sulphur dioxide, nitric acid, stannous chloride, and hydrogen peroxide. Is it necessary that an oxidising agent should contain oxygen ? *Ajmer Inter*, 1932

8. Explain what is meant by '10 volume' hydrogen peroxide. What is the strength of such a solution in grams of hydrogen peroxide per litre ?

How would you justify the statement hydrogen peroxide is an active oxidising agent ? Upon what does the oxidising power of hydrogen peroxide depend ?
Ans. 30.38

9. How is ozone prepared and obtained pure ? Describe experiments to illustrate its properties. How was its molecular weight determined ? Compare and contrast ozone and hydrogen peroxide. *Bombay* 1935

10. Describe tests to identify a gas that may either be oxygen or ozone. *Calcutta* 1953

XIX

NITROGEN AND THE ATMOSPHERE

Nitrogen

Formula N_2. Atomic number 7. Atomic weight 14.008. Boiling point −195.8°. Melting point −209.86°C. Solubility, 1 litre of water dissolves 23.5 c.c. at 0°C and 1 atmosphere.

History and Occurrence.—Nitrogen was discovered by Daniel Rutherford, but its true nature was first shown by Lavoisier (1775-76), who called it *azote*, as it did not support life (*a*, no ; *zoe*, life). It was given the name nitrogen because of its presence in nitre.

In the free state it occurs in the atmosphere to the extent of 78% by volume. In combination it is present in plants and animals, mainly as proteins. It is also found as **nitre**, also called **salt petre**, KNO_3, and as **Chile salt petre**, $NaNO_3$, in desert soils in Chile.

Laboratory preparation.—Nitrogen is prepared in the laboratory by *gently* heating a solution of *ammonium nitrite*. Instead of ammonium nitrite, a concentrated solution containing equi-molecular quantities of ammonium chloride and sodium nitrite is generally used. The solution is taken in a round bottomed flask (fig. 84) fitted with a thistle funnel and a delivery tube which dips under water in a trough, and is *gently* heated. Ammonium chloride reacts with sodium nitrite producing ammonium nitrite and sodium chloride ; the ammonium nitrite thus formed decomposes on heating, into water and nitrogen which is collected by the displacement of water.

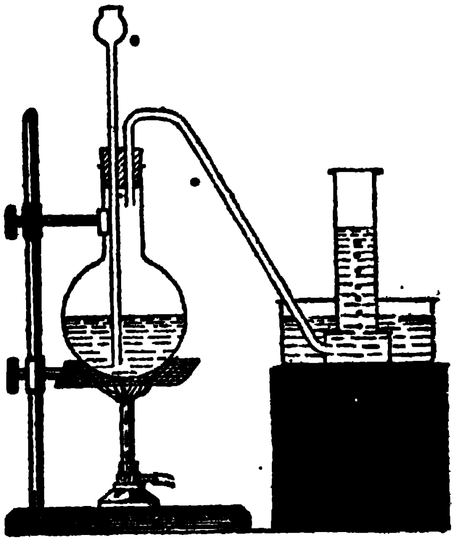


Fig. 84

$$NH_4Cl+NaNO_2=NH_4NO_2+NaCl\ ;$$

$$NH_4NO_2 = N_2+2H_2O.$$

To obtain nitrogen in the pure condition, the gas is first washed with alkali to remove traces of chlorine, then with concentrated sulphuric acid to absorb moisture and ammonia, and finally passed over heated copper filings to reduce oxides of nitrogen, and then collected over mercury.

Properties.—(i) A colourless gas without any smell or taste, nitrogen is very slightly soluble in water.

(ii) It does neither burn nor support burning. It does not turn lime water milky (*cf. carbon dioxide*). Though non-poisonous, the gas does not support respiration.

(iii) Rather inert at ordinary temperature, it enters into combination with many substances at higher temperature.

(a) **Combination with hydrogen.**—Under the influence of electric sparks nitrogen combines with hydrogen, forming ammonia. On a technical scale, they are made to combine together under a pressure of 200 atmospheres and in presence of an iron catalyst at a temperature of 550°C. $N_2 + 3H_2 \rightleftharpoons 2NH_3$.

(b) **Combination with oxygen.**—Under the influence of electric sparks at a high temperature of 3000°C nitrogen combines with oxygen to produce nitric oxide. $N_2 + O_2 \rightleftharpoons 2NO$.

(c) **Combination with metals.**—Nitrogen is absorbed by red-hot metals like calcium, magnesium and aluminium, forming nitrides. A metallic nitride on hydrolysis yields a metallic hydroxide and ammonia :

$$3Ca + N_2 = Ca_3N_2\ ;\ Ca_3N_2 + 6HOH = 2NH_3 + 3Ca(OH)_2,$$
$$3Mg + N_2 = Mg_3N_2\ ;\ Mg_3N_2 + 6HOH = 2NH_3 + 3Mg(OH)_2.$$

(d) Nitrogen is absorbed by heated (1000°C) calcium carbide giving calcium cyanamide, NCaCN, technically called **nitrolim,** which is decomposed by steam, yielding ammonia.

$$CaC_2 + N_2 = NCaCN + C\ ;\ NCaCN + 3H_2O = CaCO_3 + 2NH_3.$$

Uses of Nitrogen.—(i) Atmospheric nitrogen is fixed in large quantities as ammonia, nitric acid and nitrolim. (ii) Liquid nitrogen is a refrigerant. (iii) Nitrogen provides an inert atmosphere in certain metallurgical operations. (iv) In making gas thermometers and for filling electric bulbs. On a commercial scale nitrogen is obtained by the fractional distillation of liquid air.

Detection.—An inert gas, nitrogen is recognised by its lack of response to tests for the reactive gases. Like carbon dioxide, it does neither burn nor support burning ; but it is without action upon lime water. Nitrogen can however be absorbed by heated magnesium and can thus be distinguished and separated from argon.

Nitrogen from compounds : (i) From ammonia.—Nitrogen may be prepared by warming a paste of bleaching powder with a solution of ammonia in a flask or by dropping ammonia into sodium hypobromite solution.

$$3NaOBr + 2NH_3 = N_2 + 3NaBr + 3H_2O\ ;$$
$$3Ca(OCl)Cl + 2NH_3 = 3CaCl_2 + 3H_2O + N_2.$$

It may be obtained by passing chlorine into a strong solution of ammonia, when ammonium chloride and nitrogen are formed :

$$2NH_3 + 3Cl_2 = N_2 + 6HCl\ ;\quad 6NH_3 + 6HCl = 6NH_4Cl\ ;$$
$$\therefore\ 8NH_3 + 3Cl_2 = 6NH_4Cl + N_2$$

Ammonia must be in large excess, otherwise an explosive oily liquid, nitrogen trichloride, NCl_3, may be produced.

$$NH_3 + 3Cl_2 = NCl_3 + 3HCl.$$

(ii) **From nitric acid.**—Moderately dilute nitric acid (1 vol. conc. acid to 1 vol. water) reacts with copper turnings evolving nitric oxide, which when passed over heated copper filings yields nitrogen.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$
$$2NO + 2Cu = 2CuO + N_2.$$

(iii) **From ammonium dichromate.**—Ammonium dichromate on gentle heating, decomposes violently, evolving nitrogen. A mixture of ammonium chloride and potassium dichromate is also used. $(NH_4)_2Cr_2O_7 = N_2 + 4H_2O + Cr_2O_3$.

(iv) **From barium azide.**—Very pure nitrogen is obtained by heating barium azide to 300°C. The metal remains. $Ba(N_3)_2 = Ba + 3N_2$.

(v) **From urea.**—Nitrogen is readily evolved by the action of alkaline hypobromite solution on urea.

$$CO(NH_2)_2 + 3NaOBr = CO_2 + N_2 + 2H_2O + 3NaBr$$

(vi) **From ammonium nitrite.**—This is the most convenient method and is used for laboratory preparation.

Nitrogen from the air.—Besides traces of moisture and carbon dioxide (about 0.04 per cent by volume), air is principally a mixture of nitrogen, oxygen and argon, roughly in the proportion of 78 : 21 : 1 by volume. Nitrogen may be obtained by removing the more reactive gases from air :

(i) **By red-hot copper.**—Carbon dioxide and moisture are first removed by passing the air through strong caustic potash solution and concentrated sulphuric acid in succession. The purified air is then passed through a long tube containing red-hot copper filings which fix the oxygen as oxide of copper and nitrogen passes out ; the gas may be collected over water : $2Cu + O_2 = 2CuO$.

Nitrogen, thus obtained from air, contains about 1 per cent argon.

(ii) **By means of phosphorus.**—A porcelain crucible containing a piece of phosphorus is floated on water, and covered with a bell-jar (fig. 85) which is graduated and fitted with stopper. The phosphorus is ignited by means of a hot wire and the stopper immediately inserted. Phosphorus burns in the oxygen of air, forming white fumes of phosphorus pentoxide which dissolve in water. Water gradually rise up in the bell-jar to fill one-fifth its volume—the remaining four-fifths are filled with the residual gas. A lighted taper inserted in it is found to be extinguished ; the residual gas is therefore nitrogen. The experiment shows that air contains nitrogen and oxygen roughly in the ratio of 4 : 1 by volume.

(iii) At the room temperature oxygen may be removed from air by the action of moist iron filings, alkaline pyrogallate solution, or cuprous chloride dissolved in strong ammonia solution or an acid solution of chromous chloride. The experiment with alkaline pyrogallate is carried out as follows.—

A long glass tube closed at one end and divided into six parts by rubber bands, is filled with alkaline pyrogallate solution up to one-sixth its volume. The tube is then closed with a rubber stopper and well shaken—the liquid becomes black due to absorption of oxygen. On opening the tube under water, one of the remaining five divisions is filled with water—the residual four-fifths of original volume of air is nitrogen.

Active nitrogen.—Active nitrogen is obtained by subjecting a stream of nitrogen, drawn through a tube at 2 mm. pressure, to the action of condensed electric discharge—the gas passing beyond the discharge glows with a yellow light. A trace of impurities like oxygen or mercury vapour, appears necessary in its production. The active nitrogen is very reactive and directly combines with non-metals such as sulphur and iodine and many metals like sodium and mercury. With acetylene, it yields hydrocyanic acid. Its reactivity is due to the presence of free atoms and activated molecules of nitrogen. Active nitrogen was discovered by Lord Rayleigh in 1911.

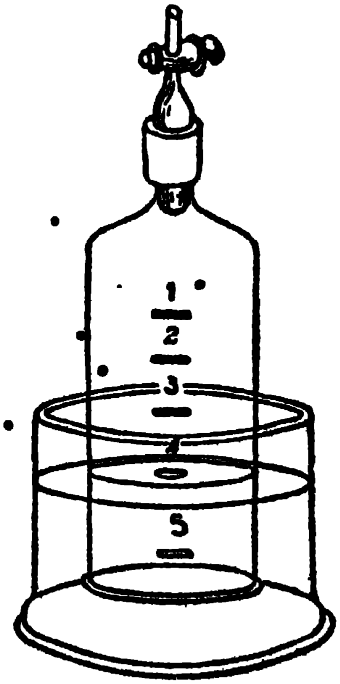


Fig. 85

The Atmosphere

One litre of air at N.T.P. weight 1.293 gms. Density of air (H = 1) is 14.44.

Constituents of Air.—Air was regarded as an element by the ancient philosophers. The discovery of oxygen and nitrogen in air by Priestley and Scheele in 1774 led Lavoisier to establish in 1775 that air was a mixture of these two gases with traces of water vapour and carbon dioxide. Besides these gases, air contains the inert gases helium, neon, argon, krypton and xenon, discovered by Raleigh and Ramsay in 1894. Ozone, ammonia, nitric and nitrous acids, sulphur dioxide, dust particles, etc. also occur in air in minute traces.

The average percentage composition of ordinary air by volume is : nitrogen 77.16 ; oxygen 20.60 ; water vapour 1.40 ; argon and other inert gases 0.80 ; carbon dioxide 0.04.

The average composition of air, freed from moisture carbon dioxide, is :

	By volume	By weight
Nitrogen	78.06	75.5
Oxygen	21.00	23.2
Inert gases	0.94	1.3

The detailed average composition of *dry* air by volume is : nitrogen 78.09 ; oxygen 20.95 ; argon 0.9323 ; CO_2 0.03 ; hydrogen 0.0000005 ; neon 0.0018 ; helium 0.0005 ; krypton 0.0001 ; ozone 0.00005 ; xenon 0.000009.

Air is a mixture.—That air is a mixture and not a compound of nitrogen and oxygen is evident from the following facts :

(i) The composition of air, freed from moisture and carbon dioxide, is *nearly* but not *entirely constant*—slight variation in the proportion of nitrogen and oxygen in air is observed in different localities and at different times. The composition of a compound, on the other hand, is definitely *fixed and invariable.*

Percentage of oxygen by volume in air in : Berlin 20.960—20.973 ; Paris 20.913—20.999 ; Calcutta 20.105—20.385.

(ii) There is *no thermal change* nor is there any volume change when nitrogen and oxygen are mixed together in the proportion as they are present in air and the mixture behaves like ordinary air, while an accompanying heat change and often a volume change occur in chemical reactions between gases.

(iii) The properties of air are those of a mixture of nitrogen and oxygen, i.e., the properties of the components of air are additive, as obtains in a mixture. Moreover a mixture of nitrogen and oxygen, if made in the proportion as they are present in air, shows all the properties of ordinary air.

(iv) If air were a compound, its molecular formula, as deduced from the percentage composition, would have been $N_{15}O_4$ (or a multiple of this) and hence its vapour density is 137.

The percentage of nitrogen and oxygen by weight in air are 75.5 and 23.2 respectively and hence the ratio of

$$\frac{\text{atoms of nitrogen}}{\text{atoms of oxygen}} = \frac{75.5/14}{23.2/16} = \frac{5.393}{1.450} = \frac{15}{4}$$

$\therefore$ the simplest formula for air is $N_{15}O_4$.

But it is actually found by experiments to be 14.4, which corresponds to a mixture of nearly 4 volumes of nitrogen and 1 volume of oxygen thus : $100 \times d = 80 \times 14 + 20 \times 16$;

$$\therefore \; d = 14.4, \text{ where } d = \text{density of air } (H = 1).$$

(v) The composition of air may be altered and its constituents partially separated by physical means, such as (a) *diffusion* and (b) *solution in water :* This is characteristic of a mixture only—a compound would diffuse or dissolve as a whole.

(a) When air is allowed to diffuse through a porous membrane of unglazed porcelain, nitrogen, being lighter than oxygen, passes out more rapidly than oxygen, causing a partial separation of the constituents of air.

(b) When air is shaken with water, the dissolved air becomes richer in oxygen than the undissolved air, since oxygen is more soluble in water than nitrogen.

The dissolved air expelled by boiling the water contains nitrogen and oxygen approximately in the ratio of 2 : 1 by volume, as against 4 : 1 in normal air.

(vi) The constituents of air may be separated by the fractional distillation of liquid air. A compound would distil as a whole.

Constituents of Air, their detections and functions.—(i) **Oxygen.**—Nitric oxide (which is a colourless gas) forms reddish brown fumes of nitrogen dioxide when exposed to air, showing that air contains free oxygen. $2NO + O_2 = 2NO_2$.

When mercury is heated in air for a long time, some red scales are formed ; these red scales decompose on being more strongly heated into mercury and a gas which responds to the tests for oxygen. Hence its presence in air.

$$2Hg + O_2 \leftrightharpoons 2HgO.$$

Oxygen supports combustion and respiration. Respiration is the transfer of oxygen of air to all parts of the body where it is required. It is carried as an unstable compound of oxygen and hæmoglobin (present in red blood corpuscles), called *oxy-haemoglobin*, by circulation of blood via lungs through different arteries. The oxygen oxidises the tissues of the animal body—with the formation of carbon dioxide and water vapour and simultaneous liberation of energy. The hæmoglobin is restored back to the lungs where it again begins the cycle as oxygen-carrier. The energy liberated maintains the heat of the body and accounts for the mechanical work it performs.

Carbon dioxide passes via veins into the lungs from where it is exhaled out. Respired air, blown through lime water, turns it milky, showing that carbon dioxide is formed during respiration. Hence *respiration is but slow combustion.* Following figures (in percentages by volume) are instructive :

		Air (inspired)	Air (expired)		
Nitrogen	...	79.00	79.02		
Oxygen	...	20.96	16.158	loss	4.75%
Carbon dioxide	...	0.04	4.42	gain	4.33%

(ii) **Nitrogen.**—The residual gas, left after the removal of oxygen by burning phosphorus, moist iron filings, heated copper turnings, etc., does not support combustion and is absorbed by heated magnesium, hence it is nitrogen. The residual gas, left after the absorption of nitrogen by heated magnesium, contains the inert gases argon, etc. Nitrogen dilutes the oxygen of air and hence moderates the process of combustion.

(iii) **Carbon dioxide.**—When exposed to air, clear lime water is covered with a white crust of calcium carbonate on its surface due to the absorption of carbon dioxide, hence air contains the gas. $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$.

Carbon dioxide forms the chief food material for plants.

(iv) **Water Vapour.**—Fused calcium chloride exposed on a watch-glass to air soon becomes *moist* owing to the absorption of water vapour from the atmosphere.

The deposition of moisture on the outside of a glass-beaker containing ice, also shows the presence of water vapour in air.

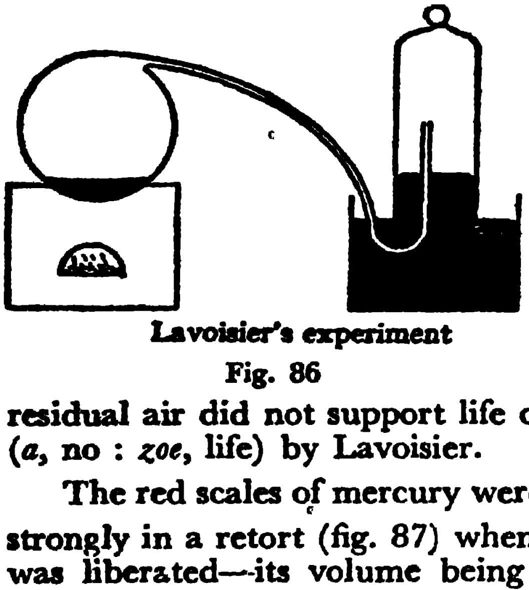
Water vapour by alternate formation of clouds and rains supports plant and animal life. It also controls the evaporation of water from the surface of the earth.

Volumetric composition of air.—Lavoisier's experiments.— The composition of air by volume was determined by the French savant Lavoisier (1743—1794) by his classical experiments on calcination of metals in air which he began in 1772.

In one of his experiments Lavoisier heated a known weight of tin in a *sealed* retort containing air and found that the weight of the retort with its contents remained unchanged after the heating, though a part of the tin was calcined. On opening the retort, air rushed in and the retort was then found to weigh more. The calcined mass of tin was then taken out of the retort and weighed. It was found to gain in weight. The increase in weight of the retort was found to be equal to the increase in weight of the mass of calcined tin. Hence he concluded that the increase in weight of calcined tin was due to the absorption of a part of air.

To find out the nature of air used up in the calcination of tin Lavoisier carried out the following famous experiment in 1775—76.

Lavoisier heated a weighed quantity (about 4 oz.) of mercury in a glass retort the neck of which communicated with a measured volume of air in a bell-jar standing over mercury (fig. 86). Red scales (mercuric oxide) were formed and found floating on the surface of mercury in the retort and the level of mercury gradually rose up in the bell-jar during heating—the level became steady after 12 days. The residual air in the bell-jar occupied four-fifths the total volume of air taken. The residual air did not support life or combustion. It was called **azote** (*a*, no : *zoe*, life) by Lavoisier.



Lavoisier's experiment

Fig. 86

The red scales of mercury were collected, weighed and heated very strongly in a retort (fig. 87) when a gas was liberated—its volume being equal to one-fifth that of the original air in the apparatus and was exactly equal to the diminution in volume of the air in the first experiment.

This gas supported life and combustion ; it was called **oxygen** by Lavoisier. When this gas was mixed with azote (residual air) ordinary air was obtained. From these two experiments Lavoisier concluded that :

(i) air is a mixture of two gases, azote (nitrogen) and oxygen, in the approximate ratio of 4 : 1 by volume.

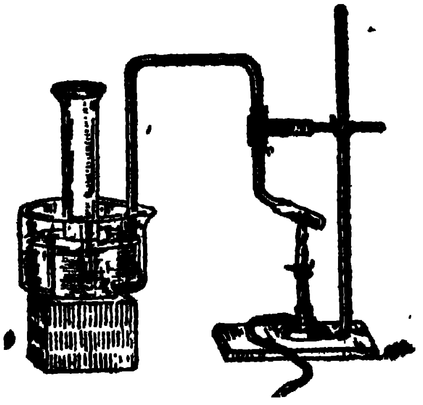


Fig. 87

(ii) oxygen of air alone supports combustion and respiration.

The classical experiment of Lavoisier on the composition of air contradicted the phlogiston theory (p. 6), which was, therefore, rejected.

The percentage by volume of oxygen in air is accurately found out by exploding a measured volume of air with excess of hydrogen in an eudiometer over mercury. The oxgyen unites with the hydrogen to form water which condenses to a liquid of negligible volume—the contraction is noted. *One-third* of the contraction equals the volume of oxygen.

Let the volume of air $= v_1$ c.c.
Vol. of air + H_2 $= v_2$ c.c.
Vol. after contraction $= v_3$ c.c.

$\therefore$ contraction due to formation of water $= (v_2-v_3)$ c.c.

Now, water contains H_2 and O_2 in the ratio of 2 : 1 by volume.

$\therefore$ vol. of O_2 in v_1 c.c. air = one-third of contraction $= (v_2-v_3)/3$;

$\therefore$ % of O_2 in air $= (v_2-v_3) \times 100/3v_1$ c.c.

The oxygen in a measured volume of air may be removed by alkaline pyrogallate and the contraction noted.

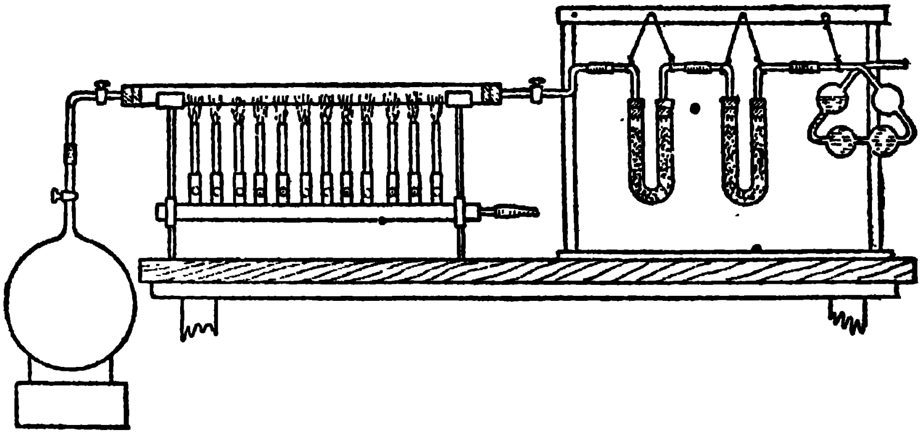


Fig. 88

Gravimetric composition of air.—Dumas' experiment.—Dumas (1841) determined the composition of air *by weight* in the following way : A long hard glass tube (fig. 88), fitted with a stop-cock at each end, is filled with copper turnings, evacuated, weighed, and then laid in a furnace. The tube is connected at one end with a weighed vacuous globe, closed by a stop cock, and at the other with two U-tubes, one (next to the tube) containing fused calcium chloride and the other solid caustic potash, and a bulb containing potash solution, which remove moisture and carbon dioxide from the air.

The tube is heated to redness and the stop-cocks are then *slightly* opened when air *slowly* passes over the heated copper. Oxygen is absorbed by the heated copper and the nitrogen passes into the vacuous globe. When the experiment is over, (as indicated by the stoppage of bubbling of air through the potash bulb), the stop-cocks are closed and the apparatus allowed to cool.

The globe is then weighed and the weight of nitrogen contained in it found out. The tube containing the copper and copper oxide is then weighed. The *nitrogen remaining in the tube* is then pumped out and the evacuated tube weighed again and the weight of nitrogen remaining in the tube determined. The weight added to that in the globe gives the total weight of nitrogen. The increase in weight of the evacuated tube gives the weight of oxygen.

Calculation : Let the weight of vacuous globe $= w_1$ gm.
Wt. of globe + nitrogen $= w_2$ gm.
$\therefore$ Wt. of nitrogen in the globe $= (w_2 - w_1)$ gm.
Wt. of evacuated tube + Cu $= w_3$ gm.
Wt. of tube + Cu + CuO + N_2 $= w_4$ gm.
Wt. of evacuated tube + Cu + CuO $= w_5$ gm.
$\therefore$ Wt. of nitrogen in the tube $= (w_4 - w_5)$ gm.
$\therefore$ Total wt. of $N_2 = (w_2 - w_1) + (w_4 - w_5)$ gm. $= W_1$ gm.
Wt. of $O_2 = (w_5 - w_3)$ gm. $= W_2$ gm.
Wt. of air = wt. of N_2 + wt. of O_2 $= (W_1 + W_2)$ gm.
$\therefore$ % of $O_2 = 100W_2/(W_1 + W_2)$; % of $N_2 = 100W_1/(W_1 + W_2)$.

Actual experiments show that the ratio, oxygen : nitrogen = 22.92 : 77.08. Allowing for the presence of 0.93 per cent of argon by volume, the composition of air by weight is : Oxygen 23.2 per cent ; Nitrogen 75.5 per cent ; Argon, etc. 1.3 per cent.

Estimation of moisture and carbon dioxide in air.—The moisture and carbon dioxide in air may be determined by aspirating a known volume of air through previously weighed calcium chloride tubes to absorb moisture, and then through weighed tubes containing solid caustic potash to absorb carbon dioxide—the increases in weight of calcium chloride and potash tubes give the measure of moisture and carbon dioxide respectively.

But carbon dioxide is generally estimated by shaking a known volume of air with standard baryta solution, and then titrating the excess baryta with a standard oxalic acid solution.

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O.$$

Air and the plant and animal life.—(a) **Oxygen and carbon dioxide.**—Due to the respiration of plants and animals (oxygen is inhaled and carbon dioxide exhaled during respiration), the combustion of carbonaceous fuel and the decay of organic matter, the amount of carbon dioxide in air gradually tends to increase with the consequent decrease in amount of the oxygen in the atmosphere. But the percentages of carbon dioxide and oxygen in air are practically constant. This constancy is due to the simultaneous removal of carbon dioxide in the following way :

(i) Carbon dioxide forms a chief food material for plants. In presence of sunlight, moisture and the green colouring matter of plants, called *chlorophyll*, the plants decompose carbon dioxide into carbon and oxygen—carbon the plants assimilate and convert into *carbohydrates* and the oxygen is restored back to air, and hence the proportion of oxygen in air is maintained constant. The net result of the change may be represented as :

$$CO_2 + H_2O + \text{energy of light} = \text{carbohydrate} + O_2.$$

(ii) A large amount of carbon dioxide is removed from the air by the *weathering of rocks*, such as felspars which are attacked by carbon dioxide :

$$K_2O,\ Al_2O_3,\ 6SiO_2\ \text{(potash felspar)} + CO_2 + 2H_2O$$
$$= K_2CO_3 + 4SiO_2 + Al_2O_3,\ 2SiO_2,\ 2H_2O\ \text{(china clay)}.$$

(iii) Sedimentary rocks such as limestone and dolomite also absorb carbon dioxide from the air, forming soluble bicarbonates which are carried into the oceans.

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2.$$

(b) **Nitrogen cycle in nature.**—Nitrogen is an essential constituent of vegetable and animal tissues but neither can directly absorb nitrogen from air, excepting a few *leguminous plants*, such as pea, bean and clover, which can directly assimilate nitrogen through the agency of *symbiotic bacteria* living on their roots, and certain algai, fungi and mosses which can also utilise elementary nitrogen.

But the following is the most important process of nitrogen-assimilation by plants. During electric discharges in the atmosphere nitrogen is converted into nitric oxide which is then oxidised by the excess of air into nitrogen dioxide. This reacts with rain water forming nitric acid which is washed down by rains to the soil where it is converted into soluble nitrates by bases present in the soil.

$$N_2+O_2 = 2NO \; ; 2NO+O_2 = 2NO_2 \; ; \; 3NO_2+H_2O = 2HNO_3+NO.$$

This 'fixed nitrogen' as soluble nitrates is absorbed from the soil by the plants through their roots. The plants in their turn convert this inorganic nitrogen into complex nitrogenous organic substances, called *proteins*. The nitrogen of air is thus utilised by plants in the form of nitrates. It is estimated that no less than 250,000 tons of nitric acid are produced daily by electric discharges.

Animals, on the other hand, can only make use of nitrogen built into proteins in the plant body. Hence the herbivorous animals feed upon plants for their nitrogen supply ; carnivorous animals acquire their necessary nitrogen by consuming proteins in other animals. As a result of the above processes, the nitrogen content of air gradually tends to decrease.

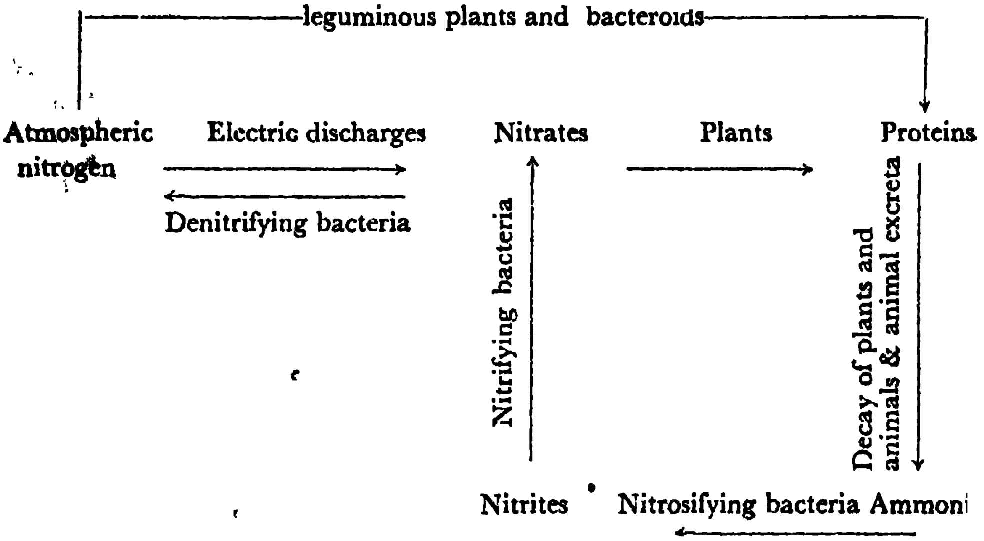
But much of the nitrogen consumed by animals is restored to the soil in the form of urea in the excreta—urea is readily hydrolysed to ammonia and carbon dioxide : $CO(NH_2)_2+H_2O = CO_2+2NH_3$. Also when the animal and plant bodies undergo decay or the animal excreta putrefy, most of the organic nitrogen (proteins) is liberated as ammonia which is oxidised in the soil by the combined action of *nitrosifying* and *nitrifying bacteria* into nitrate to be again assimilated by plants. A portion of the fixed nitrogen is set free by the action of *denitrifying bacteria* in the soil. This process takes place in such a way in nature as to maintain the proportion of nitrogen in air practically constant.

The circulation of nitrogen from inorganic compounds in the soil to proteins in plants and animals and back again is known as nitrogen cycle.

A supply of fixed nitrogen to the soil is essential for the life of plants and animals. In primitive communities the natural processes for fixation of nitrogen by leguminous plants and by lightning, led to a gradual accumulation of available nitrogen in the soil ; but in civilised communities in modern times much fixed nitrogen is lost by disposing sewage to the sea, and this loss is compensated mainly by fixing atmospheric nitrogen as ammonia.

Fixation of atmospheric nitrogen.—As stated above, only a small amount of the nitrogen, fixed by the natural process of electric discharges, falls on fertile soil and is utilised by plants—most of it is lost into the sea and thereby becoming unavailable for the direct use of plants. Hence the necessity of increasing the available nitrogen content in the soil. This may be done (i) by rotation of crops, whereby corn, which depletes the soil of nitrogen, is followed by the cultivation of a leguminous plant such as clover which replenishes it, and (ii) by dressing the soil with nitrogeneous compounds, mainly as ammonium sulphate or sodium nitrate, to the soil. Farmyard manure containing nitrogeneous animal products is also used.

THE NITROGEN CYCLE



It is estimated that about 80 per cent of world's total output of nitrogeneous compounds are used as fertilisers and the rest 20 per cent for the manufacture of explosives, and alkali cyanides used in the extraction of gold and silver.

The two natural sources for 'fixed nitrogen' are (i) ammoniacal liquor from the gas works from which ammonia is recovered as sulphate to be used as a fertiliser and (ii) Chile saltpetre, $NaNO_3$. But they meet only about 20 and 5 per cents respectively of the total requirements—the rest 75 per cent is obtained by '*fixing*' the atmospheric nitrogen by artificial processes as (a) *ammonia* (Haber process), (b) *nitric acid* (Birkeland-Eyde process), (c) *calcium cyanamide*, technically called *nitrolim* (Franc-Caro process), and (d) *aluminium nitride* (Serpek process). The methods (a) and (c) only are technically important.

XX

COMPOUNDS OF NITROGEN

Ammonia

Formula NH_3. Vapour density 8.5. Boiling point $-33.4°$. Melting point $-77.7°$. Critical temperature 132.5°.

Occurrence.—Ammonia is a product of the decomposition of organic matter containing nitrogen. The stable manure, for example, contains urea, $CO(NH_2)_2$, derived from the urine of animals. The urea is converted by the action of bacteria into ammonium carbonate which slowly decomposes, yielding ammonia, and hence its smell in a stable, and its presence in traces in air.

$$CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3 ; \ (NH_4)_2CO_3 = 2NH_3 + H_2O + CO_2$$

Laboratory preparation.—Ammonia is prepared by the action of a strong base, such as lime or caustic soda, upon ammonium salt. An intimate mixture of ammonium chloride (1 part) and dry slaked lime (3 parts) is used in the laboratory. The mixture is heated in a flask or a hard glass test-tube (fig. 89)—the evolved ammonia is dried by passing through a tower filled with lumps of quick lime and then collected in gas jars by the *downward* displacement of air or over mercury :

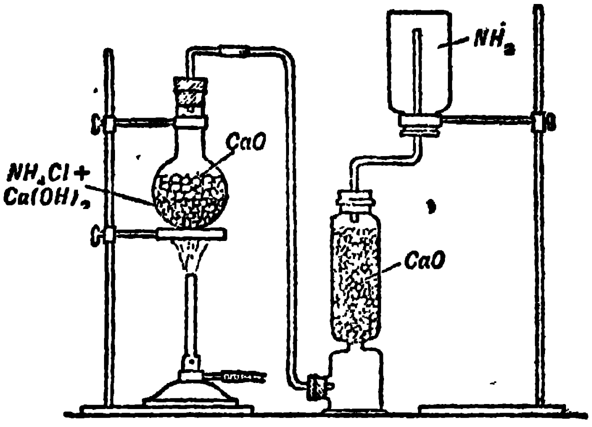


Fig. 89

$$2NH_4Cl + Ca(OH)_2 \quad CaCl_2 + 2NH_3 + 2H_2O.$$

Drying of ammonia.—The gas cannot be dried by strong sulphuric acid or phosphorus pentoxide which itself absorbs ammonia that is basic, yielding ammonium sulphate or phosphate. Calcium chloride also absorbs the gas forming a compound $CaCl_2$, $8NH_3$ and hence also unsuitable as a drying agent. **Ammonia is dried by quick lime which itself is basic.**

A supply of ammonia is readily obtained in the laboratory by allowing liquor ammonia to fall in drops from a dropping funnel into a flask constaining solid sticks of caustic soda.

Properties.—(i) Ammonia is a colourless gas with a pungent smell (odour of smelling-salt) and is *lighter than air*. The gas is readily liquefied by pressure alone (6 atmospheres at 10°).

Expt.—An *empty* jar (i.e., containing air) is inverted over a jar of ammonia and the lid is removed. Ammonia, being lighter than air, travels in the upper jar—tested by introducing a glass rod moistened with concentrated hydrochloric acid when dense white fumes of ammonium chloride are evolved.

(ii) It is the most soluble of all gases—1 volume of water at 0°C dissolves 1150 volumes of ammonia to give a solution containing 47% ammonia by weight. A saturated solution of sp. gr. 0.88 contains only 35% ammonia. The concentrated solution is know as **liquor ammonia fortis.** *A bottle of liquor ammonia should be carefully opened after cooling in ice, as there is always a high pressure inside.*

The solution of ammonia is alkaline to litmus. The solubility in water and the alkalinity of the solutions are shown by the *fountain experiment* :

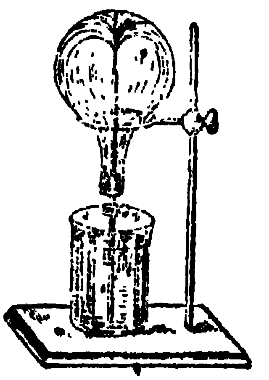
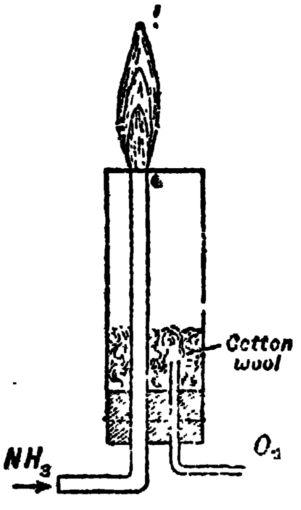


Fig. 90

Fountain experiment.—A round bottomed flask (fig. 90) is filled with dry ammonia and closed with a cork through which passes a long tube provided with a stop cock—one end of the tube drawn into a jet, is inside the flask and the other dips in red litmus solution. The stop cock is opened and a little ether is poured upon the flask which evaporates, causing local cooling and ammonia contracts as a result thereto, producing partial vacuum and hence the red litmus solution rushes in the form of a fountain inside the flask. The solution turns blue. Hence ammonia is soluble in water and the solution is alkaline.

(iii) It does not support combustion, nor does it burn in air, but in oxygen it burns with a greenish-yellow flame, forming nitrogen and water :



Fif. 91

$$4NH_3 + 3O_2 = 6H_2O + 2N_2.$$

Expt.—Dry ammonia is slowly passed through a tube surrounded by a wider tube containing a plug of cotton wool through which diffuses a stream of oxygen (fig. 91)—on ignition, the ammonia readily burns in the oxygen with a greenish-yellow flame.

(iv) In presence of platinum gauze as a catalyst, heated to 500°C, a mixture of ammonia with air or oxygen is oxidised to nitric oxide :

$$4NH_3 + 5O_2 = 6H_2O + 4NO$$

(v) Basic in character, it neutralises acids, yielding ammonium salts : $NH_3 + HCl = NH_4Cl$;

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

Expt.—A piece of paper soaked in concentrated hydrochloric acid is put in a jar of ammonia—dense white fumes of ammonium chloride are formed.

(vi) Ammonia is a mild reducing agent. Ammonia is oxidised to nitrogen and water when passed over heated lead monoxide or cupric oxide : $2NH_3 + 3CuO = 3Cu + N_2 + 3H_2O$.

Chlorine decomposes ammonia liberating nitrogen ; with excess of chlorine the explosive oily liquid nitrogen trichloride is formed :

$$2NH_3+3Cl_2 = N_2+6HCl \ ; \quad 2NH_3+6Cl_2 = 2NCl_3+6HCl.$$

Iodine reacts with a solution of ammonia, yielding the black explosive compound, nitrogen iodide, NI_3, NH_3.

(vii) Ammonia reacts with the alkali metals at red-heat, forming amides, such as sodamide. Water decomposes sodamide, yielding ammonia back :

$$2Na+2NH_3 = 2NaNH_2+H_2. \quad NaNH_2+H_2O = NaOH+NH_3.$$

(viii) When ammonia is dissolved in water, it forms the hydrate ammonium hydroxide which dissociate into ammonia and hydroxyl ions : $NH_3+H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$.

The presence of free ammonia in the solution is recognised by its smell. The existence of hydroxyl ions is shown by the alkalinity of the solution and also by its power of precipitating many metallic hydroxides by interaction with the soluble salts of the metals ; e.g.

$$AlCl_3+3NH_4OH = Al(OH)_3+3NH_4Cl \ ; \quad FeCl_3+3NH_4OH = Fe(OH)_3+3NH_4Cl$$

In some cases the precipitated hydroxide redissolves in excess of ammonia solution ; e.g., copper sulphate gives a pale blue precipitate of basic copper sulphate which dissolves in excess of the precipitant forming a deep blue solution :

$$2CuSO_4+2NH_4OH = CuSO_4,Cu(OH)_2+(NH_4)_2SO_4.$$

$$CuSO_4,Cu(OH)_2+(NH_4)_2SO_4+6NH_4OH=2[Cu(NH_3)_4]SO_4+8H_2O.$$

Silver nitrate solution gives a white precipitate which quickly passes into brown oxide, soluble in excess of ammonia.

$$2AgNO_3 + 2NH_4OH = Ag_2O + 2NH_4NO_3 + H_2O.$$

$$Ag_2O + 4NH_3 + H_2O = 2[Ag(NH_3)_2]OH.$$

Liquid ammonia dissolves sodium and potassium to give deep blue solutions.

Tests.—Ammonia is detected by the following properties : (a) its characteristic pungent smell and alkaline reaction, i.e., by the blueing of moist red litmus paper ; (b) it forms dense white fumes of ammonium chloride with gaseous hydrochloric acid ; (c) it produces a yellow or brown colouration or a precipitate with *Nessler's reagent* (an alkaline solution of potassium mercuric iodide, K_2HgI_4). This is the most delicate test for ammonia and ammonium salts : (d) it blackens a piece of paper soaked in mercurous nitrate solution.

Uses.—(i) Huge quantities of ammonia are used in the manufacture of *fertilizers*, such as *ammonium sulphate*, and ammonium phosphate, and *nitrochalk* (one part $CaCO_3$ + 1 part NH_4NO_3) ; *nitric acid* by the Ostwald process, *sodium carbonate* by the Solvay process, and urea, $CO(NH_2)_2$.

(ii) Liquid ammonia is used as a refrigerant in ice-making.

(iii) Ammonia is transported in cylinders and then 'cracked' (i.e., decomposed into its elements by heat) to supply hydrogen for the purposes of welding and cutting of metals.

(iv) Ammonia and ammonium salts are used in medicine—'smelling salt' contains solid ammonium carbonate and a little lime water.

(v) Ammonia is used as cleansing agent for removing grease and as a reagent in laboratories.

Because of its easy volatility and high latent heat of vapourisation liquid ammonia is used as a refrigerant in ice-making. By means of a compression pump anhydrous ammonia gas is condensed to liquid in *condensing coils* cooled by a stream of cold water to remove the heat generated as a result of compression. Liquid ammonia then passes through an expansion valve into *expansion coils*, immersed in brine in a tank, wherein it vaporises due to release of pressure. During vaporisation the temperature of brine goes down below 0°C, thus causing the water kept in cans in the brine tank to freeze into ice. From the expansion coils the ammonia gas passes once again into the compression pump, and the process repeats, figure 92.

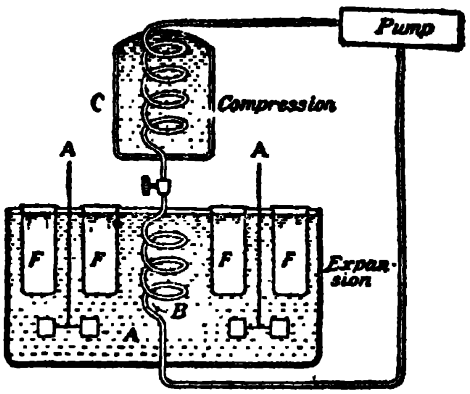


Fig. 92

Ammonia by other methods.—(i) by the reduction of the oxides of nitrogen ; e.g., by passing a mixture of nitric oxide and hydrogen over heated spongy platinum :

$$2NO + 5H_2 = 2NH_3 + 2H_2O.$$

(ii) By heating a solution of a nitrate or nitrite with zinc and strong caustic soda solution : $NaNO_3 + 8H = NaOH + NH_3 + 2H_2O$.

(iii) By heating a metallic nitride with an alkali :

$$Mg_3N_2 + 6HOH = 3Mg(OH)_2 + 2NH_3$$

$$AlN + NaOH + H_2O = NaAlO_2 + NH_3.$$

These methods are not suitable for the laboratory preparation of ammonia.

Manufacture of ammonia.—(i) **Gasworks ammonia.**—Ammonia is obtained as a by-product in the manufacture of coal-gas. Coal contains about 1—1.5 per cent nitrogen and also some hydrogen. When coal is subjected to destructive distillation for the manufacture of coal-gas, the nitrogen is converted mainly into ammonia which collects in the *ammoniacal liquor* as an aqueous solution—the liquor containing both free ammonia and ammonium salts. The liquor is heated with steam to drive out the free ammonia, and the residue is then treated with milk of lime and additional steam to liberate the ammonia from its salts. The ammonia is absorbed in 60 per cent sulphuric acid, yielding crystals of ammonium sulphate, mostly used in agriculture as a fertiliser.

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

The yield is about 20—25 lbs. of ammonium sulphate per ton of coal.

(ii) **Synthetic ammonia : Haber's process. Synthesis of** ammonia from its elements is utilised in the Haber's process :

$$N_2+3H_2 \rightleftharpoons 2NH_3+2\times 11{,}000 \text{ calories.}$$

The reaction is *exothermic* (i.e., attended with evolution of heat) and reversible. The yield of ammonia diminishes with rise of temperature. The reaction should, therefore, be conducted at a low temperature (p. 117). But at a low temperature the speed of the reaction is slow, and hence the reaction is carried out at an *optimum temperature* at which the speed of the reaction is not too slow, nor the yield of ammonia too low. *The optimum temperature is about* 500°C *in the Haber's process.*

The speed of the reaction is increased by using a catalyst—*finely divided iron* with 'promoters' such as traces of molybdenum, or a mixture of aluminium oxide and potassium oxide, is the catalyst used.

The formation of ammonia takes place with a contraction in volume and hence it is favoured at high pressures (p. 117). A pressure of 200 *atmospheres* is employed in the Haber's process.

The table shows how the yield of ammonia depends on temperature and pressure—equilibrium percentages by volume of ammonia are as follows :

Temperature	10	100	200	1000 atm. pressure.
400°C	3.85	25	36.3	80
500°	2.1	10.6	17.6	57.5
550°	0.76	6.8	12.0	41
600°	0.5	4.5	8.3	31.5

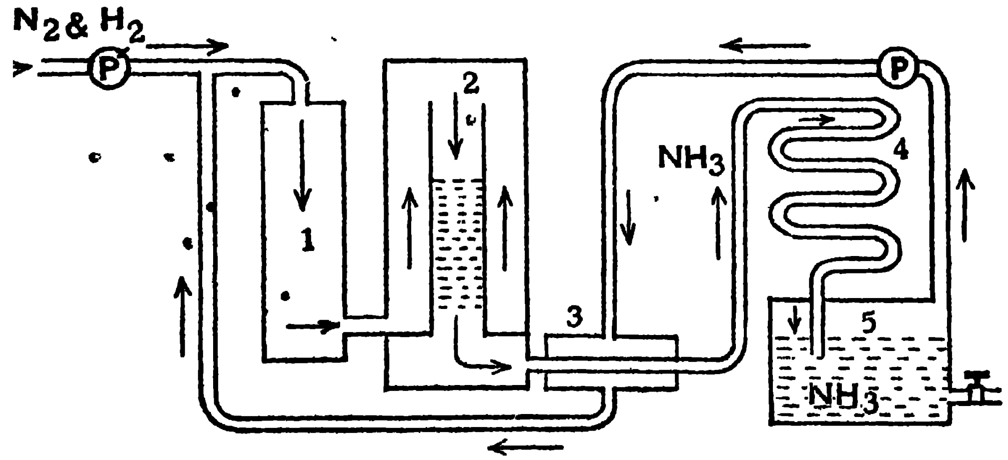


Fig. 93

A mixture of pure and dry nitrogen and hydrogen in the ratio of 1 : 3 by volume is compressed to 200 atmospheres and sent by means of a pump P' via a sodalime drying chamber (1) into the catalyst chamber (fig. 93) which is a tube (2) of chrome-vanadium steel. The gases first circulate around the outside of the central tube (2) and thereby get preheated and and then pass down the tube containing trays of promoted catalyst kept at 550° by being heated electrically ; but once the reaction starts external heating is unnecessary. Nitrogen and hydrogen react to yield ammonia. The reaction is exothermic, and hence the incoming mixture of nitrogen and hydrogen is circulated round the catalyst-tube for maintaining the optimum temperature.

The gases leaving the catalyst chamber contain about 12% ammonia and the rest unconverted nitrogen and hydrogen, and pass through a heat-interchanger (3) to preheat the entering gases. The ammonia formed is removed by absorption in water, and for this the cooled gas is brought in contact with water in washers (5) *while still under high pressure*, producing a 25% solution of ammonia. The unreacted nitrogen and hydrogen are circulated by a pump P via the heat-interchanger (3) and are dried in the soda-lime tower, and these together with more nitrogen and hydrogen, are recirculated by a pump P′ to the catalyst chamber and so the process continues.

The unreacted nitrogen and hydrogen, instead of being recirculated, are blown off from time to time to remove the argon which unavoidably enters the plant with the nitrogen.

A pressure of 900 atmospheres is used in Claude's process—in high pressure processes ammonia is removed by cooling and liquefaction under pressure.

The required mixture of nitrogen and hydrogen is usually made from :

(a) the nitrogen obtained from liquid air by fractionation and the hydrogen prepared electrolytically.

(b) a mixture of water gas ($CO + H_2$) and producer gas ($CO + N_2$)—these gases in correct proportion are mixed with excess steam and passed over a heated catalyst (mixture of $Fe_2O_3 + Cr_2O_3$) at 450°C (p. 187), when CO is oxidised to CO_2, thus $CO + H_2O \leftrightharpoons CO_2 + H_2$. The CO_2 is removed by absorption with water under pressure and last traces of CO by washing with ammoniacal cuprous formate solution under 200 atmospheres—the pure nitrogen-hydrogen mixture is ready for the process ; the method was used in original Haber plant.

There is a Haber plant in Mysore State. The Sindri Fertiliser project has gone into operation to produce ammonia by the Haber process, getting the nitrogen-hydrogen mixture from *air, coal and steam.*

The ammonia may be absorbed in a suspension of crushed calcium sulphate (calcined gypsum) in water and carbon dioxide passed into the liquid—the precipitated calcium carbonate is filtered off and ammonium sulphate is crystallised out from the filtrate ; a process extensively utilised commercially. Ammonia is thus converted into ammonium sulphate without using sulphuric acid.

$$2NH_3+CO_2+H_2O+CaSO_4 = (NH_4)_2SO_4+CaCO_3.$$

Ammonium sulphate is produced by this method in the Sindri fertiliser plant.

(iii) **Cyanamide Process.**—Heated calcium carbide absorbs nitrogen, yielding calcium cyanamide, thus : $CaC_2 + N_2 = NCaCN$ (calcium cyanamide) + C.

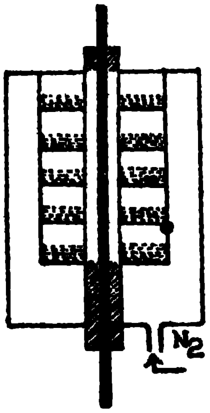


Fig. 94

The cyanamide furnace is a refractory-lined sheet iron cylinder, with a thin carbon rod passing through the centre. Fig. 94. A cardboard tube is placed round the carbon rod and the crushed calcium carbide is packed in with cardboard partitions at intervals. The cardboard tube and partition burn up during the operation and leave openings for the circulation of nitrogen. On passing electric current through the carbon rod, the temperature rises to about 800°C ; pure nitrogen, freed from moisture and oxygen, is then fed in at the base, under pressure, and the reaction yielding calcium cyanamide takes place. The reaction is exothermic and the temperature of the mass rises to 1100°C. When no more nitrogen is absorbed, the sintered mass is cooled.

The dark grey product thus obtained is called **nitrolim.** It is wetted with water to decompose any unconverted carbide and is then hydrolysed in autoclaves, i.e., pressure digesters, into which steam is passed under a pressure of 3 atmospheres, yielding ammonia and calcium carbonate.

Ammonia is driven out by increasing the pressure gradually to about 11 atmospheres : $NCaCN + 3H_2O = 2NH_3 + CaCO_3$.

Ammonia is no longer manufactured by this process ; but the nitrolim is prepared to be used directly as a fertiliser, since it slowly liberates ammonia in the soil.

Volumetric composition of ammonia : (i) Eudiometric method.—The method depends upon the decomposition of ammonia into nitrogen and hydrogen by continued electric sparks. Dry and pure ammonia is collected in an eudiometer (fig. 95) over mercury—its volume measured—and then subjected to series of electric sparks until no further increase in volume takes place. The final volume after due adjustment of the mercury levels is found to be *double* the original volume.

An excess of oxygen is then passed into the eudiometer and the mixture again sparked when the hydrogen is oxidised into water resulting in a contraction in volume which is noted. The residual gas in the eudiometer is nitrogen and the oxygen left unused.

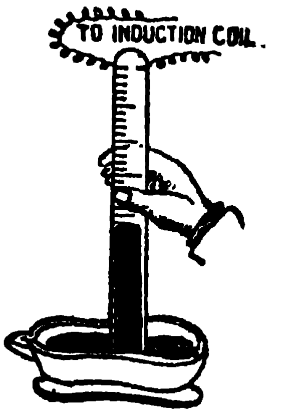


Fig. 95

Taking 2 volumes of ammonia, the volume after sparking becomes four. The contraction after sparking with the excess of oxygen becomes 4½ volumes ; of this two-thirds, namely 3 volumes, is due to hydrogen, and hence nitrogen occupies 1 volume only. Hence :

1 volume nitrogen + 3 volumes hydrogen = 2 volumes of ammonia.

∴ 1 molecule nitrogen + 3 molecules hydrogen = 2 molecules ammonia, by Avogadro's hypothesis.

Or, ½ mol. nitrogen + 1½ mol. hydrogen = 1 mol. ammonia.

i.e., 1 molecule of ammonia contains 1 atom of nitrogen and 3 atoms of hydrogen, since molecules of nitrogen and hydrogen are diatomic, and hence the formula is NH_3. This is *confirmed* by the experimentally found vapour density of the gas 8.5, which show that the molecular weight is 17.

(ii) **Hofmann's method.**—The method depends upon the liberation of nitrogen by the interaction between ammonia and chlorine gas :

$$2NH_3+3Cl_2 = 6HCl+N_2 \; ; \quad 6NH_3+6HCl = 6NH_4Cl.$$

A long graduated glass tube (fig. 96), fitted with a stop-cock at one end and a dropping funnel at the other, and marked off into three equal volumes *by rubber rings*, is filled with chlorine gas. Excess of a concentrated solution of ammonia is cautiously and gradually added from the funnel to the chlorine in the tube which decomposes ammonia liberating nitrogen.

Ammonia reacts vigorously with the chlorine, giving flashes of yellowish-green flame and forming white fumes of ammonium chloride, and hence the tube is cooled by dipping in a tall jar of water.

The excess ammonia is then neutralised by adding dilute sulphuric acid. The top of the funnel is then closed and the stop-cock at the bottom is opened in the jar of water—water fills the tube up to two-thirds only. The remaining one volume is occupied by a gas which is found to be nitrogen.

Hydrogen and chlorine combine in equal volumes to form hydrogen chloride : $H_2+Cl_2 = 2HCl$.

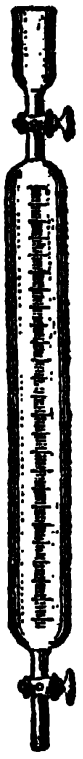


Fig. 96

The three volumes of chlorine must have combined with three volumes of hydrogen derived from ammonia which simultaneously liberates one volume of nitrogen, filling only one division of the tube. Hence, ammonia is made up of 1 volume of nitrogen and 3 volumes of hydrogen.

1 volume of nitrogen is combined in ammonia with 3 volumes of hydrogen.

Suppose n molecules of nitrogen are contained in 1 volume of nitrogen.

Then, n mols of nitrogen combine with 3n mols of hydrogen to give ammonia.

$\therefore$ 1 mol. of nitrogen combines with 3 mols of hydrogen to give ammonia.

Or 2 atoms of nitrogen combine with 6 atoms of hydrogen to give ammonia.

i.e., the ratio of number of nitrogen atoms to number of hydrogen atoms is 2 : 6, i.e., 1 : 3, in ammonia, and hence the formula for ammonia is $(NH_3)x$.

The vapour density of ammonia is found by experiments to be 8.5, and hence the molecular weight is 17. $\therefore$ $(NH_3)x = 17$, or $(14 + 3)x = 17$, $\therefore$ $x = 1$.

Gravimetric composition of Ammonia.—The method depends upon the oxidation of ammonia by heated copper oxide, thus :

$$3CuO + 2NH_3 = 3Cu + N_2 + 3H_2O.$$

A hard glass tube containing copper oxide followed by copper gauze, is connected to weighed calcium chloride tubes and a weighed exhausted globe. The copper is used to reduce oxides of nitrogen, if any be produced.

$$5CuO + 2NH_3 = 5Cu + 2NO + 3H_2O \; ; \; 2Cu + 2NO = 2CuO + N_2$$

The tube is heated in a furnace, and a measured volume of dry ammonia gas (the weight of which under the given conditions is calculated from the normal density) is slowly passed through the tube.

The water formed is absorbed in the calcium chloride tubes, and the weight of hydrogen is calculated. The nitrogen passing on is collected in the globe, and its weight found out. In this way the ratio of the weight of nitrogen to that of hydrogen is found to be 14 : 3. This is in the ratio of 1 atom of nitrogen to 3 atoms of hydrogen, and hence the formula for ammonia is $(NH_3)x$.

$\therefore$ $(NH_3)x = 2 \times 8.5$, the vapour density of ammonia is 8.5,

i.e., $(14 + 3)x = 17$, or $x = 1$; $\therefore$ formula is NH_3.

Ammonium Salts

Ammonia is a very weak base but it reacts with acids, yielding ammonium salts which are stable compounds. The ammonium salts contain the *ammonium radical* NH_4, which behaves like an alkali metal. The ammonium salts are often very similar to and isomorphous with the corresponding salts of the alkali metals, particularly potassium, but they differ in their actions towards heat and alkali. Alkali liberates ammonia from ammonium salts :

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2NH_3 + 2H_2O.$$

Certain ammonium salts decompose while many others dissociate on heating : $NH_4NO_3 = N_2O + 2H_2O$; $NH_4Cl \rightleftharpoons NH_3 + HCl$.

Ammonium salts may be prepared by neutralising ammonia with acids, but they are generally prepared from ammonium sulphate obtained by neutralising by-product ammonia from gas works with sulphuric acid.

Ammonium chloride or **sal-ammoniac.** NH_4Cl, was first prepared by the Arabs by heating camel's dung. It may be obtained by distilling a mixture of common salt and ammonium sulphate, when ammonium chloride sublimes, or by neutralising ammonia with hydrochloric acid. $2NaCl + (NH_4)_2SO_4 = Na_2SO_4 + 2NH_4Cl$.

A white crystalline solid with a saline taste, it is soluble in water with a considerable lowering of temperature. It dissociates on heating into ammonia and hydrochloric acid : $NH_4Cl \rightleftharpoons NH_3 + HCl$.

Its use in tinning and soldering depends on dissociation—the hydrogen chloride formed cleanses the metal surface by dissolving oxide films and thus enables the solder to 'bite' firmly. It also finds applications as a reagent in the laboratory, in dry cells, in medicine, and in dyeing and calico printing.

Ammonium sulphate.—It may be prepared by passing ammonia gas into 60 per cent sulphuric acid or by passing ammonia into a suspension of gypsum in water and then passing carbon dioxide through the liquid (p. 233).

$$CaSO_4 + 2NH_3 + CO_2 + H_2O = CaCO_3 + (NH_4)_2SO_4$$

It forms transparent crystals isomorphous with potassium sulphate and is very soluble in water.

Besides its use as a laboratory reagent, it finds uses in the preparation of other ammonium salts. It is extensively used as a fertiliser in agriculture.

Ammonium nitrate, NH_4NO_3.—It is prepared by neutralising ammonia with 60% nitric acid or by double decomposition of ammonium sulphate and sodium nitrate in aqueous solution.

$$(NH_4)_2SO_4 + 2NaNO_3 = Na_2SO_4 + 2NH_4NO_3.$$

Sodium sulphate separates first from the hot solution—ammonium nitrate crystallises out on cooling. A white crystalline solid, freely soluble in water, ammonium nitrate decomposes on heating into nitrous oxide and water : $NH_4NO_3 = N_2O + 2H_2O$.

It is liable to detonation if stored in bulk. The high explosive *ammonal* and *amatol* are the mixtures of ammonium nitrate with aluminium and T.N.T. respectively.

Ammonium nitrite, NH_4NO_2, may be made by evaporating a solution of ammonium chloride and sodium nitrite in vacuum and subliming in vacuum. $NH_4Cl + NaNO_2 = NH_4NO_2 + NaCl$.

An explosive deliquescent solid, it decomposes by heat into nitrogen and water. $NH_4NO_2 = N_2 + 2H_2O$.

A solution of a mixture of sodium nitrite with ammonium chloride or sulphate is used for the preparation of nitrogen.

Ammonium carbonate or **sal-volatile,** $(NH_4)_2CO_3$.—It is prepared by heating a mixture of ammonium sulphate and well-ground chalk, when ammonium carbonate sublimes :

$$(NH_4)_2SO_4 + CaCO_3 = CaSO_4 + (NH_4)_2CO_3.$$

The sublimate is largely a mixture of ammonium bicarbonate NH_4HCO_3, and ammonium carbamate, $NH_2CO.ONH_4$, with some normal carbonate $(NH_4)_2CO_3$, but in solution the carbamate is hydrolysed to normal carbonate : $NH_2CO.ONH_4 + H_2O = (NH_4)_2CO_3$.

The normal carbonate is obtained as a white crystalline solid by digesting the commercial carbonate, *sal volatile,* with concentrated aqueous ammonia at low temmature, 12°C, for several hours.

It is used as a reagent in the laboratory and in medicine in *smelling salt.*

Yellow ammonium sulphide.—When hydrogen sulphide is led into concenasted ammonia (liquor ammonia) solution diluted with 4 times its volume of water, a solution of ammonium hydrosulphide, NH_4HS results—the solution on digestion with flowers of sulphur yields *yellow ammonium sulphide* solution whih contains ammonium polysulphide $(NH_4)_2Sx$. The colourless ammonium hydrosulphide solution on exposure to air, turns yellow due to liberation of sulphur whichdissolves in the excess of hydrosulphide to give yellow ammonium sulphide solution.

$$NH_3 + H_2S = NH_4HS \text{ ; } NH_4HS + O \text{ (air)} = NH_3 + H_2O + S$$

$$2NH_3 + H_2S + xS = (NH_4)_2Sx \text{ (yellow ammonium sulphide).}$$

The yellow ammonium sulphide solution deposits sulphur on acidification. It dissolves sulphides of As, Sb and Sn and hence its use as a reagent in the laboratory.

Tests.—(i) Ammonium salts when warmed with caustic soda or soda lime give the characteristic pungent smell of ammonia.

(ii) Ammonium salts give a yellow or brown colour or a precipitate with Nessler's reagent.

Hydroxylamine, NH_2OH.—It is a *base* and forms salt with acids, e.g., hydroxylamine hydrochloride, $NH_2OH.HCl$. The salts are made by :

(a) *The reduction of nitric oxide with nascent hydrogen :* $NO + 3H = NH_2OH$ Nitric oxide is passed through flasks containing tin and concentrated hydrochloric acid. Hydroxylamine hydrochloride is formed and also some ammonium chloride. The tin is precipitated with hydrogen sulphide and filtered off—the filtrate is evaporated to dryness and extracted with absolute alcohol, which dissolves out the $NH_2OH.HCl$ but not NH_4Cl. The hydroxylamine hydrochloride is precipitated from the alcoholic solution by ether.

(b) *The reduction of nitrite with sodium sulphite.*—Sulphur dioxide is slowly passed into a cold solution containing sodium nitrite and sodium carbonate at −2°C, until just acid. The sodium salt of hydroxylamine sulphonic acid is formed. This, on keeping at 90° for 2 days in presence of dilute sulphuric acid, yields hydroxylamine sulphate, $(NH_3OH)_2SO_4$. It is crystallised out after neutralising with sodium carbonate.

$$NaNO_2 + 3NaHSO_3 = HO.N(SO_3Na)_2 + Na_2SO_3 + H_2O.$$
$$HO.N(SO_3Na)_2 + 2H_2O = HO.NH_2 + 2NaHSO_4.$$

(c) *The electrolytic reduction of nitric acid.*—$HNO_3 + 6H = NH_2OH + 2H_2O$. A lead anode is separated by a porous pot from an amalgamated lead beaker (which is the cathode) cooled in ice. The cathode and anode compartments contain fifty per cent sulphuric acid. Hydroxylamine sulphate is formed on adding 50 per cent nitric acid drop by drop to the cathode compartment.

Pure hydroxylamine is made by the action of sodium methoxide on hydroxylamine hydrochloride in methyl alcohol solution.

$$HO.NH_2.HCl + CH_3ONa = NH_2OH + NaCl + CH_3OH.$$

The precipitated sodium chloride is filtered off and the filtrate is distilled under reduced pressure (40 mm.) when methyl alcohol distils first and then hydroxylamine.

It forms colourless, deliquescent crystals, m. p. 33°. It decomposes explosively on heating, giving nitrogen, ammonia and nitrous oxide :

$$3NH_2OH = N_2 + NH_3 + 3H_2O \;;\; 4NH_2OH = N_2O + 2NH_3 + 3H_2O.$$

The aqueous solution is *a weaker base than ammonia* and prepicipitates many metallic hydroxies (Zn, Al, etc.) : $NH_2OH + H_2O \rightleftharpoons NH_3OH^+ + OH^-$,

It is a strong reducing agent, precipitating cuprous oxide from alkaline solutions of copper salts (Fehling's solution) and metallic gold from its salts, and reducing acid solutions of ferric salts to the ferrous state—nitrous oxide is formed at the same time. It also reacts quantitatively with iodine.

$$2NH_2OH + 4CuO = 2Cu_2O + N_2O + 3H_2O$$
$$2NH_2OH + 4FeCl_3 = 4FeCl_2 + N_2O + 4HCl + H_2O.$$
$$2NH_2OH + 2I_2 = 4HI + N_2O + H_2O$$

In *alkaline* solution ferrous compounds are *oxidised* to the ferric state and ammonia is formed :

$$NH_2OH + 2Fe(OH)_2 + H_2O = 2Fe(OH)_3 + NH_3.$$

Hydroxylamine reacts with hydrogen peroxide, evolving oxygen :

$$NH_2OH + H_2O_2 = NH_3 + H_2O + O_2$$

With nitrous acid hydroxylamine gives nitrous oxide, and with nitric acid it evolves nitric oxide on warming.

$$NH_2OH + HNO_2 = N_2O + 2H_2O \;;\; NH_2OH + HNO_3 = 2NO + 2H_2O$$

In absence of water hydroxylamine shows feeble acid properties, e.g., it forms a calcium compound $(H_2NO)_2Ca$.

Hydrazine, N_2H_4.—It is made by boiling ammonia solution with a solution of sodium hypochlorite in presence of a little glue which prevents the oxidation of ammonia to nitrogen. Chloramine, NH_2Cl, first formed, reacts with excess ammonia to give hydrazine.

$$NH_3 + NaOCl = NH_2Cl + NaOH \;;\; NH_3 + NH_2Cl = N_2H_4 + HCl.$$

The solution is then acidified with dilute sulphuric acid and the hydrazine sulphate, $N_2H_4.H_2SO_4$, crystallised out. The hydrazine sulphate is then distilled under reduced pressure with strong caustic potash solution in a glass apparatus avoiding cork or rubber connections, when *hydrazine hydrate* is obtained as a colourless fuming liquid. This on distillation over solid caustic potash or barium oxide gives *anhydrous hydrazine*, a colourless liquid, b.p. 113.5° and m.p. 1.4°.

It is soluble in water and alcohol. It readily absorbs moisture and carbon-dioxide from the air, and is poisonous. It inflames in dry oxygen, readily reacts with halogens, and splits on heating.

$$N_2H_4 + 2I_2 = N_2 + 4HI \; ; \; 3N_2H_4 = N_2 + 4NH_3$$

It is a very weak base (weaker than ammonia) and forms salts which are hydrolysed in solution.

It is a powerful reducing agent, precipitating gold, silver and platinum from their salts, and reducing Fehling's solution to cuprous oxide and ferric salts to ferrous salts :

$$4CuO + N_2H_4 = 2Cu_2O + 2H_2O + N_2$$

It reacts quantitatively with iodine in presence of sodium bicarbonate or with permanganate in presence of dilute sulphuric acid.

$$N_2H_4 + 2I_2 = 4HI + N_2 \; ; \; N_2H_4 + 2O = N_2 + 2H_2O.$$

Hydrazoic acid, N_3H.—The sodium salt of hydrazoic acid (sodium azide) is made by passing nitrous oxide over heated (to 190°) sodamide—the water formed acting on a part of the sodamide to form ammonia :

$$NaNH_2 + N_2O = N_3Na + H_2O \; ; \quad NaNH_2 + H_2O = NaOH + NH_3.$$

The sodamide is first made by passing ammonia over fused sodium at 150°—250°.

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

The sodium azide on distillation with 50 per cent sulphuric acid gives a solution of hydrazoic acid. The solution is fractionated, dried with fused calcium chloride and finally distilled, when pure hydrazoic acid is obtained as a colourless mobile liquid, b.p. 37°. *It is dangerously explosive and poisonous.*

It dissolves in water forming a corrosive acid liquid in which it is only slightly ionised : The solution dissolves many metals (Zn, Cu, Fe) evolving nitrogen :

$$N_3H \leftrightharpoons N_3' + H^+ \; ; \qquad Zn + 3N_3H = Zn(N_3)_2 + N_2 + NH_3.$$

The azides of alkali metals evolve pure nitrogen on heating : $2N_3Na = 2Na + 3N_2$. Azides of heavier metals are explosive, lead azide, $Pb(N_3)_2$, being used as a detonator. The soluble azides give a white precipitate of silver azide, N_3Ag, soluble in ammonia, and a blood-red colour with ferric chloride which is discharged by HCl (cf. thiocyanate). The hydrazoic acid is formulated as $N \equiv N = NH$.

Oxides and oxyacids of nitrogen

The chief oxides and oxyacids of nitrogen are the following :

Nitrous oxide, N_2O	Hyponitrous acid, $H_2N_2O_2$
Nitric oxide, NO	
Nitrogen trioxide, N_2O_3.	Nitrous acid, HNO_2
Nitrogen tetroxide, N_2O_4,	$N_2O_4 \leftrightharpoons 2NO_2$
or nitrogen dioxide, NO_2	
Nitrogen pentoxide, N_2O_5	Nitric acid, HNO_3

All the oxides of nitrogen are endothermic at room temperature.

Nitrous oxide, N_2O (Laughing gas).

History.—The gas was discovered by Priestly in 1772 by the action of moist iron filings upon nitric oxide : $2NO + Fe + H_2O = N_2O + Fe(OH)_2$.

But it was carefully studied by Davy in 1799 who gave it the name *laughing gas*, since it caused hysteric laughter on inhalation.

Preparation.—Nitrous oxide is prepared in the laboratory by *cautiously* heating (below 200°C) dry ammonium nitrate (or a mixture of ammonium sulphate and sodium nitrate) in a flask fitted with a cork and a delivery tube—*overheating may lead to explosion of the ammonium nitrate* (fig. 84). The nitrate decomposes, yielding nitrous oxide and water :

$$(NH_4)_2SO_4 + 2NaNO_3 = Na_2SO_4 + 2NH_4NO_3.$$
$$NH_4NO_3 = N_2O + 2H_2O.$$

The gas is collected over **hot water** or mercury, since it is appreciably soluble in cold water (0.78 vol. in 1 vol. of water at 15°).

Purification.—The gas produced by the above reaction contains moisture, nitrogen, higher oxides of nitrogen, ammonia and chlorine (due to the presence of a little ammonium chloride in the nitrate) as impurities. It is carefully *purified* by passing successively through (i) caustic potash solution to absorb chlorine and nitrogen dioxide, (ii) ferrous sulphate solution to absorb nitric oxide, and (iii) concentrated H_2SO_4 to remove moisture and ammonia, and then collected over mercury—the gas, however, contains a little nitrogen. The purified gas is liquified by compression in steel cylinders.

Very pure nitrous oxide is obtained by mixing solution of hydroxylamine hydrochloride and sodium nitrite : $NH_2OH, HCl + NaNO_2 = NaCl + N_2O + 2H_2O$.

Nitrous oxide is also formed by reducing NO with sulphur dioxide or dilute HNO_3 with zinc or by boiling nitric acid with stannous chloride (in HCl) solution.

$$2NO + SO_2 + H_2O = H_2SO_4 + N_2O.$$
$$4Zn + 10HNO_3 = Zn(NO_3)_2 + 5H_2O + N_2O.$$
$$2HNO_3 + 4SnCl_2 + 8HCl = 4SnCl_4 + 5H_2O + N_2O.$$

Nitrous oxide is not readily synthesised but may be obtained by passing an electric discharge through a mixture of nitrogen and oxygen at low pressure. It is an endothermic compound : $N_2 + \frac{1}{2}O_2 = N_2O - 19{,}700$ cals.

Properties.—(i) A colourless neutral gas with a faint but pleasant smell, nitrous oxide is fairly soluble in *cold water* and more so in alcohol but *insoluble in hot water*. The solution has no action on litmus ; hence it is a neutral oxide and does not behave as the anhydride of hyponitrous acid, which, however, yields nitrous oxide on decomposition : $H_2N_2O_2$ (hyponitrous acid) $= N_2O + H_2O$.

(ii) It produces hysteric laugher on inhalation and hence the name **laughing gas**—but continued inhalation causes insensibility to pain and finally death.

(iii) It does not burn but *resembles oxygen in supporting combustion* of the burning substances and *relighting a glowing splint*, since it readily decomposes above 600°C, yielding a gas containing one-third its volume of oxygen : $2N_2O = 2N_2 + O_2$. Nitrous oxide supports combustion more vigorously than air.

Burning pieces of phosphorus, charcoal, sulphur, and heated metals such as sodium, potassium and iron wire, burn brilliantly in the gas—the heat decomposing the gas with the liberation of oxygen which supports combustion. It is also reduced by heated copper.

$$5N_2O + 2P = P_2O_5 + 5N_2 ; \quad 2N_2O + S = SO_2 + 2N_2.$$
$$N_2O + 2Na = Na_2O + N_2 ; \quad N_2O + Cu = CuO + N_2.$$

Both nitrous oxide and oxygen are *colourless gases ;* both support combustion viogorously and *rekindle a glowing splint.*

But nitrous oxide **differs from oxygen** in the following respects :

Properties	Nitrous oxide	Oxygen
(i) Density (H = 1)	22	16
(ii) Odour	Faint sweet odour.	Odourless.
(iii) Solubility in (a) water	Fairly soluble in *cold* water (1.3 c.c. per c.c. of water at 0°) ; insoluble in *hot* water.	Scarcely soluble.
(b) alcohol	Fairly soluble (4.18 c.c. per c.c. of alcohol at 0°).	Much less soluble than nitrous oxide.
(iv) Solubility in alkaline pyrogllate	Nil.	Readily absorbed.
(v) Reaction with nitric oxide	No reaction	Reddish-brown fumes of NO_2.
(vi) Burning white phosphorus is inserted in the gas jars ; combustion over, the jars are inverted over water	Phosphours burns brilliantly. Water does not rise up in the jar, since equal volume of N_2 is is liberated. $5N_2O+2P=P_2O_5+5N_2$	Phosphorus burns brilliantly. Water rises up and fully fills the jar, since the O_2 is completely absorbed. $4P + 5O_2 = 2P_2O_5$.

Use of nitrous oxide.—It is used as a mild anæsthetic in dental and other minor surgical operations. The gas for this purpose must be pure and is administered along with about 10% oxygen.

Nitric Oxide, NO.—**Preparation.**—The gas was first investigated by Priestley in 1772. Nitric oxide is usually prepared in the laboratory by the action of copper turnings upon cold dilute nitric acid (1 vol. concentrated acid + 1 vol. water). Copper turnings are taken in a Woulfe's bottle fitted with a thistle funnel and a delivery tube, and covered with a layer of water. On pouring concentrated nitric acid down the funnel, nitric oxide is liberated which forms reddish-brown fumes of nitrogen peroxide with the air in the bottle. The brown fumes are allowed to escape and the colourless gas is collected over water :

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

Purification.—The gas so obtained is not pure ; it contains the impurities nitrogen and nitrous oxide. It is *purified* by absorbing it in cold saturated solution of ferrous sulphate (when the dark brown nitroso compound [Fe(NO)]SO_4 is formed)—the dark brown solution on heating yields nearly pure nitric oxide which may be dried by sulphuric acid and collected over mercury :

$$FeSO_4 + NO \rightleftharpoons [Fe(NO)]SO_4.$$

Nitric oxide is formed in small quantities at very high temperature by direct synthesis : $N_2 + O_2 \leftrightharpoons 2NO - 2\times21{,}600$ calories.

Nearly pure nitric oxide is formed : (i) by heating a mixture of dilute sulphuric acid, ferrous sulphate and potassium nitrate, or (ii) by the action of ferrous chloride in acid solution on sodium nitrate :

$$2HNO_3 + 6FeSO_4 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO.$$

$$3FeCl_2 + NaNO_3 + 4HCl = 3FeCl_3 + NaCl + 2H_2O + NO.$$

Very pure nitric oxide is obtained : (i) by the action of acidified solution of potassium iodide on sodium nitrite :

$$2NaNO_2 + 2KI + 4HCl = 2NaCl + 2KCl + I_2 + 2H_2O + 2NO.$$

or (ii) by shaking mercury with a solution of potassium nitrate and conc. sulphuric acid :

$$2KNO_3 + 4H_2SO_4 + 6Hg = K_2SO_4 + 3Hg_2SO_4 + 2NO + 4H_2O.$$

Properties.—(i) A colourless, poisonous gas, it is slightly heavier than air and only slightly soluble in water. *It is a neutral oxide like nitrous oxide.*

(ii) It does not burn nor does it ordinarily support burning. Compared with nitrous oxide (decomposing at 600°C) nitric oxide decomposes at 1000°C. Hence only vigorously burning phosphorus or boiling sulphur burn in the gas—the heat being sufficient to decompose nitric oxide, yielding oxygen : $2NO = N_2 + O_2$.

Feebly burning phosphorus, burning sulphur and charcoal or a lighted taper are extinguished in the gas : $4P + 10NO = 2P_2O_5 + 5N_2$.

(iii) It readily unites with oxygen, yielding reddish brown fumes of nitrogen dioxide : $2NO + O_2 = 2NO_2$.

(iv) It is **absorbed** by cold ferrous sulphate solution to yield a dark brown liquid containing the unstable nitroso-compound, (Fe.NO)SO_4, which decomposes on heating, liberating nitric oxide.

$$FeSO_4 + NO \rightleftharpoons (Fe.NO)SO_4.$$

NO is rapidly absorbed by alkaline sodium or potassium sulphite solution, forming dinitroso sulphite, $Na_2(NO)_2SO_3$, which at once evolves N_2O on acidification :

$$Na_2(NO)_2SO_3 = Na_2SO_4 + N_2O.$$

(v) It reacts with chlorine in presence of charcoal yielding nitrosyl chloride : $2NO + Cl_2 = 2NOCl$.

(vi) It may be reduced to ammonia, when heated with hydrogen in presence of platinum : $2NO + 5H_2 = 2NH_3 + 2H_2O$.

It is reduced to hydroxylamine by tin and hydrochloric acid, and to nitrous oxide by sulphurous acid.

$$NO + 3H = NH_2OH \; ; \qquad 2NO + H_2SO_3 = N_2O + H_2SO_4.$$

Like other oxides of nitrogen, it may be reduced to nitrogen by heated metals like sodium, potassium, iron, copper and nickel :

$$2Cu + 2NO = 2CuO + N_2 \; ; \qquad 2Ni + 2NO = 2NiO + N_2.$$

A mixture of nitric oxide and carbon disulphide vapour, made by shaking few drops of carbon disulphide in a jar of nitric oxide, when ignited burns with a brilliant blue flame :

$$2CS_2 + 10NO = 2CO + 4SO_2 + 5N_2.$$

Nitric oxide is thus an oxidising agent. But a powerful oxidising agent like potassium permanganate oxidises nitric oxide to nitric acid —the permanganate is reduced to a colourless solution ; here nitric oxide acts as a reducing agent :

$$6KMnO_4+9H_2SO_4+10NO = 3K_2SO_4+6MnSO_4+4H_2O+10HNO_3.$$

Iodine also oxidises nitric oxide into nitric acid :

$$3I_2 + 4H_2O + 2NO = 2HNO_3 + 6HI.$$

Nitric oxide is used as a carrier of oxygen in the manufacture of sulphuric acid by the chamber process.

Composition of nitrous oxide and nitric oxide.—The following methods are available.—(i) **Thumb tube method.**—Gay-Lussac and Thenard (1811) determined the compositions of nitrous oxide and nitric oxide by heating *potassium* in a measured volume of the gas. The pure gas (nitrous oxide or nitric oxide) is collected by the displacement of mercury in a bent tube standing on mercury—(fig. 97)—the volume of the gas is noted. A piece of potassium is then inserted into the tube and heated in the gas when the potassium combines with the oxygen, setting nitrogen free—on cooling, the volume of the gas which is found to be nitrogen is noted.

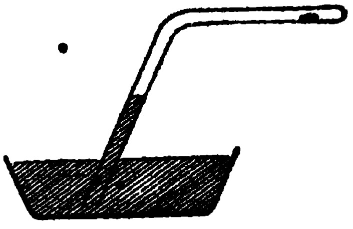


Fig. 97

(ii) The composition may also be determined by heating a spiral of *iron wire* in a measured volume of the gas when it unites with oxygen, setting nitrogen free. A graduated tube is fitted at one end with a cork through which pass a pair of platinum wires connected together by a spiral of iron wire inside the tube. The tube stands in a trough of mercury—the volume of the gas is noted. The iron wire is then heated electrically by connecting the platinum wires with the terminals of a battery. The iron wire combines with the oxygen, liberating nitrogen whose volume is noted after adjustment of mercury levels.

Experimental Results :—(i) **Nitrous oxide.**—It is found that the volume of the gas remains unaltered, i.e., nitrous oxide contains its own volume of nitrogen. Hence,

1 volume nitrous oxide contains 1 volume nitrogen.

∴ 1 mole nitrous oxide contains 1 mole nitrogen, (by Avogadro's hypothesis).

Hence, the formula is N_2Ox and the molecular weight $= 28 + 16x$.

But the mol. wt. $= 2 \times 22 = 44$, the vapour density being 22,

$28 + 16x = 44 \quad \therefore \quad x = 1$. Hence the formula is N_2O.

(ii) **Nitric Oxide.**—It is found that nitric oxide contains half its volume of nitrogen. Hence,

1 volume nitric oxide contains ½ volume nitrogen.

1 mole nitric oxide contains ½ mole nitrogen, (by Avogadro's hypothesis).

∴ the formula is NOx and the mol. wt. $= 14 + 16x$.

But the mol. wt. $= 2 \times 15 = 30$, the vapour density being 15.

∴ $14 + 16x = 30$, or $x = 1$; hence the formula is NO.

(iii) The formula of nitrous oxide may be determined by exploding the gas with hydrogen in a eudiometer, (Davy, 1799). 20 c.c. of the gas are mixed with 20 c.c. of hydrogen and exploded—20 c.c. of nitrogen are found. 20 c.c. of hydrogen must have combined with 10 c.c. of oxygen to yield water. Therefore 20 c.c. nitrous oxide contain 20 c.c. nitrogen and 10 c.c. oxygen, i.e., 1 vol. nitrous oxide contains 1 vol. nitrogen and $\frac{1}{2}$ vol. oxygen and hence the formula may be deduced to be N_2O.

Nitric oxide alone does not explode with hydrogen, but if mixed with an equal volume of nitrous oxide, both the gases explode when the mixture is sparked with an equal volume of hydrogen.

Nitrogen trioxide, N_2O_3.—It may be obtained by distilling a mixture of equal weights of arsenious acid and nitric acid (60 per cent) and condensing the vapours in a receiver cooled in freezing mixture :

$$As_2O_3 + 2HNO_3 = As_2O_5 + N_2O_3 + H_2O.$$

A blue liquid at very low temperature, it dissociates giving reddish brown fumes :

$$N_2O_3 \leftrightarrows NO + NO_2.$$

It forms nitrous acid with water, and nitrite with alkali. It is thus the anhydride of nitrous acid.

$$N_2O_3 + H_2O = 2NHO_2. \qquad N_2O_3 + 2NaOH = 2NaNO_2 + H_2O.$$

Nitrogen dioxide, NO_2 and **nitrogen tetroxide,** N_2O_4.—In the laboratory the gas is prepared by heating dry lead nitrate. Powdered lead nitrate is taken in a hard glass tube, and the evolved gases, reddish brown in colour, are passed through a U-tube, cooled in freezing mixture, where nitrogen tetroxide condenses as a pale yellow liquid and the oxygen passes out—a glowing taper held at the exit of the U-tube is rekindled, (fig. 61). $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$.

The experiment may be used to prove that lead nitrate contains Pb, nitrogen and oxygen. The nitrogen peroxide is passed over copper heated to *bright* redness, when copper oxide is formed and nitrogen passes on.

$$4Cu + 2NO_2 = 4CuO + N_2.$$

The yellow residue of lead oxide is heated in a current of hydrogen, when it is reduced to metallic lead, which is soft and malleable and marks paper :

$$PbO + H_2 = Pb + H_2O.$$

Properties.—(i) Nitrogen dioxide, NO_2, is a reddish-brown, poisonous gas ; it condenses on cooling in a good freezing mixture to a pale yellow liquid (b.p. 22°) which gradually *separates* as colourless crystals (m.p. −9°) of nitrogen tetroxide, N_2O_4. It dissociates on heating into nitrogen dioxide—the dissociation is complete at 140°C.

$$N_2O_4 \rightleftharpoons 2NO_2.$$

During heating the colour deepens gradually from yellow to reddish brown—the colour change accompanies a decrease in density to 140° when the density becomes steady and corresponds with NO_2. Above 140°, again the colour becomes paler due to dissociation $2NO_2 \leftrightarrows 2NO + O_2$, and also the density decreases, until at 620° the gas is colourless when the dissociation become complete. Reverse change occurs on cooling :

$$\underset{\text{solid}}{N_2O_4} \underset{-9^\circ}{\leftrightarrows} \underset{\text{liquid}}{N_2O_4} \underset{22^\circ}{\leftrightarrows} \underset{\text{vapour}}{N_2O_4} \underset{140^\circ}{\leftrightarrows} \underset{\text{gas}}{2NO_2} \underset{620^\circ}{\leftrightarrows} 2NO + O$$

(ii) It does not burn nor support burning readily. But vigorously burning phosphorus, sulphur and charcoal burn in it. Potassium spontaneously inflames in the gas : $K + 2NO_2 = KNO_2 + NO$.

(ii) It reacts with water, yielding a colourless solution of nitrous and nitric acids, hence it is a *mixed acid-anhydride.* But the nitrous acid decomposes, giving nitric acid and nitric oxide :

$$2NO_2+H_2O = HNO_2+HNO_3 \; ; \; 3HNO_2 = HNO_3+H_2O+2NO.$$

Hence the final products are nitric acid and nitric oxide.

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

The gas is absorbed by alkali, yielding a mixture of nitrate and nitrite : $2NO_2 + 2NaOH = NaNO_2 + NaNO_3 + H_2O$.

(iv) It is a powerful oxidising agent. Thus, it liberates iodine from potassium iodide, precipitates sulphur from hydrogen sulphide :

$$2KI+NO_2+H_2O = 2KOH+NO+I_2 \; ; \; H_2S+NO_2 = H_2O+NO+S.$$

Sulphur dioxide is oxidised to sulphuric acid in presence of steam —a reaction used in the manufacture of the acid. Carbon monoxide is oxidised to carbon dioxide :

$$NO_2+SO_2+H_2O = H_2SO_4+NO \; ; \; NO_2+CO = NO+CO_2.$$

It may be reduced to nitrogen by heated metals such as sodium, iron or copper. It may also be reduced to ammonia by hydrogen in presence of platinum : $2NO_2 + 7H_2 = 2NH_3 + 4H_2O$.

Composition.—The composition of nitrogen dioxide is ascertained by passing the gas over weighed copper contained in a tube heated to *bright redness* (other-wise NO is formed)—the nitrogen liberated is collected ; its volume measured and weight calculated. The increase in weight of the tube gives the weight of oxygen :

$$4Cu + 2NO_2 = 4CuO + N_2.$$

From the weights of nitrogen and oxygen, the percentage composition of the gas is ascertained and thence its formula, which is found to be NO_2.

The formula cannot be accurately determined by volumetric methods, since the gas dissociates easily, giving a mixture of NO_2 and N_2O_4.

Nitrogen pentoxide, N_2O_5.—It is obtained by the dehydration of nitric acid by phosphorus pentoxide. Phosphorus pentoxide is added to concentrated nitric acid contained in a retort cooled in freezing mixture. The mixture on gentle distillation yields nitrogen pentoxide which condenses as colourless crystals in ice-cooled receivers.

$$2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5.$$

It may also be obtained (i) by the action of dry chlorine on gently heated silver nitrate : $4AgNO_3 + 2Cl_2 = 4AgCl + 2N_2O_5 + O_2$.

(ii) by passing ozonised oxygen into cooled liquid nitrogen tetroxide :

$$N_2O_4 + O_3 = N_2O_5 + O_2.$$

Nitrogen pentoxide forms colourless hygroscopic crystals, stable below 0°, but melts with decomposition at about 30°C to a dark-brown liquid which decomposes into red vapours of NO_2 and oxygen at 50°C : $2N_2O_5 = 2N_2O_4 + O_2$.

Phosphorus, sodium and potassium burn in liquid nitrogen pentoxide if warmed. Charcoal is not attacked by the liquid even on boiling, but it burns brilliantly in the vapour.

It dissolves in water, giving nitric acid ; hence it is the anhydride of nitric acid. It is a powerful oxidising agent.

$$N_2O_5 + H_2O = 2HNO_3.$$

Comparison of oxides of nitrogen.—(i) All the oxides are gaseous at the ordinary temperature except nitrogen pentoxide, N_2O_5, which is a colourless solid —N_2O and NO are colourless, N_2O_3 and N_2O_4 are reddish-brown.

(ii) **Solubility in water.**—N_2O is soluble in cold water, NO is slightly soluble, while the other oxides dissolve in water, yielding acids, hence they are acidic oxides. N_2O and NO are neutral.

$$N_2O_3 + H_2O = 2HNO_2 \; ; \qquad N_2O_5 + H_2O = 2HNO_3.$$
$$N_2O_4 + H_2O = HNO_3 + HNO_2.$$

(iii) **Action of alkalis.**—Except N_2O and NO which are neutral, the rest of the oxides react with alkalis.

(iv) **Combustibility,** etc.—All the oxides are non-combustible. N_2O readily supports combustion like oxygen, while the other oxides do not ordinarily support burning ; but vigorously burning phosphorus, sulphur, etc., continue burning in them—the heat being sufficient to decompose the oxides, liberating oxygen.

(v) **Absorbents.**—N_2O is absorbed by alcohol, and NO by cold ferrous sulphate solution, while the three acidic oxides are absorbed by alkalis.

(vi) **Physiological action.**—All the oxides are poisonous—N_2O is a weak anæsthetic.

Nitrous acid, HNO_2, **and nitrities.**—(i) The nitrous acid is unstable and is known only in solution. Unlike nitric acid, it is a very weak acid and can be liberated from its salts even by acetic acid. It may be obtained in solution by adding cold dilute sulphuric acid to ice-cold barium nitrite solution and filtering from barium sulphate.

$$Ba(NO_2)_2 + H_2SO_4 = BaSO_4 + 2HNO_2.$$

But at ordinary temperature the acid breaks up giving reddish brown fumes of oxides of nitrogen.

$$2HNO_2 \rightleftharpoons H_2O + N_2O_3 \rightleftharpoons H_2O + NO + NO_2.$$

A nitrite, therefore, yields reddish brown fumes on treatment with dilute acids. Nitrous acid decomposes in dilute solutions on keeping, yielding nitric acid, thus : $3HNO_2 = HNO_3 + 2NO + H_2O$.

(ii) It is a more powerful *oxidising agent* than nitric acid. Thus iodine is readily liberated when a nitrite is added to an acidified solution of potassium iodide—a blue colour is obtained on the addition of starch. This is a test for nitrous acid.

$$2KI + 2KNO_2 + 2H_2SO_4 = 2K_2SO_4 + I_2 + 2NO + 2H_2O.$$

Nitrous acid readily oxidises sulphrous acid to sulphuric acid and hydrogen sulphide to sulphur and water.

$$H_2SO_3 + 2HNO_2 = H_2SO_4 + 2NO + H_2O.$$
$$H_2S + 2HNO_2 = S + 2NO + 2H_2O.$$

It also oxidises stannous chloride to stannic chloride, and ferrous alts to ferric salts : $SnCl_2+2HCl+2HNO_2 = SnCl_4+2NO+2H_2O$.

$$2FeSO_4+H_2SO_4+2HNO_2 = Fe_2(SO_4)_3+2NO+2H_2O.$$

(iii) Unlike nitric acid, it also acts as a *reducing agent*, e.g., it reduces chlorine or bromine water and acid permanganate solution :

$$HNO_2+Br_2+H_2O = HNO_3+2HBr,$$

$$2KMnO_4+3H_2SO_4+5HNO_2 = K_2SO_4+2MnSO_4+5HNO_3+3H_2O.$$

Nitrous acid is oxidised by hydrogen peroxide :

$$HNO_2 + H_2O_2 = HNO_3 + H_2O.$$

Ammonium chloride, and also urea react with nitrous acid, yielding nitrogen—the reaction is used in removing nitrous acid from a solution :

$$NH_4Cl + HNO_2 = N_2 + 2H_2O + HCl$$

$$CO(NH_2)_2 \text{ (urea)} + 2HNO_2 = 2N_2 + 3H_2O + CO_2$$

Salts of nitrous acid, i.e., nitrites are more stable and are easily prepared. Sodium nitrite and potassium nitrite may be made by heating the corresponding nitrate, either alone or with lead.

$$2KNO_3 = 2KNO_2 + O_2 \; ; \; KNO_3 + Pb = KNO_2 + PbO.$$

Alkali nitrites are made by passing into the alkali equimolecular mixtures of NO and NO_2, i.e., N_2O_3—the latter being made by catalytic oxidation of ammonia.

$$2KOH + NO + NO_2 = 2KNO_2 + H_2O.$$

Tests for nitrite.—(i) A nitrite yields reddish brown fumes on acidification with dilute sulphuric acid.

(ii) A nitrite in acid solution liberates iodine from potassium iodide—the iodine gives blue colour with starch.

(iii) A nitrite gives a brown colour with a solution of meta-phenylene-diamine hydrochloride in hydrochloric acid.

(iv) A nitrite gives an intense pink colour with a mixture of solution of sulphanilic acid and α-naphthylamine in acetic acid. The last two tests are very delicate and are utilised for colorimetric estimation of nitrites in water.

Hyponitrous acid, $H_2N_2O_2$.—Sodium hyponitrite, $Na_2N_2O_2$, is obtained by reducing sodium nitrite solution with sodium amalgam.

$$NaON = O + 4H + O = NONa \longrightarrow NaON = NONa + 2H_2O.$$

The solution is filtered through asbestos and concentrated over strong sulphuric acid in a vacuum desiccator. when crystals of sodium hyponitrite, $Na_2N_2O_2$, $5H_2O$, deposit. They are washed with alcohol and ether, and dired in a vacuum desiccator, when a white powder of anhydrous $Na_2N_2O_2$, stable in air, is obtained. An aqueous solution of sodium hyponitrite gives a *yellow* precipitate of silver hyponitrite with silver nitrate solution.

$$Na_2N_2O_2 + AgNO_3 = Ag_2N_2O_2 + 2NaNO_3$$

Hyponitrous acid is prepared by adding silver hyponitrite to an ether solution of hydrogen chloride in absence of moisture :

$$Ag_2N_2O_2 + 2HCl = 2AgCl + H_2N_2O_2$$

The silver chloride is filtered off, and the filtrate on evaporation gives colourless crystals of hyponitrous acid, $H_2N_2O_2$.

Hyponitrous acid is also formed by the action of nitrous acid on hydroxylamine.

$$HO.NH_2 + O = N.OH \longrightarrow HO.N = N.OH + H_2O$$

The aqueous solution decomposes with evolution of nitrous oxide.

$$H_2N_2O_2 = H_2O + N_2O.$$

Nitric acid

Formula HNO_3. Density at 15°, 1.52. Boiling point 78.2°. Freezing point —41.3°.

History and Occurrence.—This acid, called **aqua fortis,** was known to the alchemists—Geber (A. D. 788) obtained it by the distillation of nitre, blue vitriol and alum. Its composition was determined by Lavoisier in 1776.

It was first obtained by distilling saltpetre with green vitriol :

$$4FeSO_4 + 4KNO_3 + 3H_2O = 2Fe_2O_3 + 4KHSO_4 + NO + NO_2 + 2HNO_3.$$

Free nitric acid, produced by lightning flashes, occurs in traces in air. It is found in the form of nitre (potassium nitrate) in the soil of tropical countries like India, and as sodium nitrate (Chile salt petre) in Chile in South America.

Laboratory preparation.—Nitric acid is volatile—a less volatile acid like sulphuric acid displaces it from a nitrate. Hydrochloric acid though stronger than sulphuric acid is not used in the preparation of nitric acid, since hydrochloric acid is volatile.

In the laboratory nitric acid is prepared by distilling a mixture of potassium or sodium nitrate with concentrated sulphuric acid, when the following reaction takes place, forming potassium (or sodium) hydrogen sulphate and evolving nitric acid vapours.

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3 ;$$
$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

Equal parts by weight of potassium nitrate and concentrated sulphuric acid are taken in a stoppered glass retort (fig. 18) the stem of which communicates with a water-cooled receiver. Nitric acid distils on moderate heating at about 200°C and collects in the receiver.

With excess of nitre and at a higher temperature of about 800°C a further reaction occurs ; the potassium (or sodium) hydrogen sulphate being converted into normal sulphate :

$$KNO_3 + KHSO_4 = K_2SO_4 + HNO_3.$$

But the reaction is not carried to this stage, as

(i) the glass retort would crack at the high temperature required ;

(ii) the normal sulphate forms a solid mass in the retort which it is difficult to remove ; and

(iii) most of the acid would decompose at the high temperature :

$$4HNO_3 = 2H_2O + 4NO_2 + O_2.$$

Properties.—(i) A colourless, fuming liquid with a choking smell, the acid is soluble in water in all proportions.

(ii) It is a *strong monobasic acid*—the acid is readily ionised in solution and is, therefore, a strong acid : $HNO_3 \rightleftharpoons H^+ + NO_3'$.

It turns blue litmus red and reacts with alkalis, yielding salt and water : $HNO_3 + NaOH = NaNO_3 + H_2O$.

The acid contains water and oxides of nitrogen formed by the decomposition of the acid as impurities, and is brown in colour. It may be concentrated up to 98% by distillation with concentrated sulphuric acid : oxides of nitrogen are removed by bubbling air through the acid till colourless. Pure nitric acid may be obtained as colourless crystals by freezing the 98 per cent acid at—42°C.

(iii) It is a *highly corrosive liquid* and produces painful blisters if it comes in contact with skin which it attacks, causing a yellow stain, Other organic bodies like leather, silk, etc., are also stained yellow by strong nitric acid.

Cotton which is almost pure cellulose, is converted into *nitro-cellulose* by the action of concentrated HNO_3 in presence of concentrated H_2SO_4—the nitrocellulose is employed under the name of *gun-cotton* in explosives. Glycerine under similar conditions, produces *nitro-glycerine*, also called *Nobel's oil* which is absorbed in kieselguhr for making *dynamite*..

Oil of turpentine bursts into flame with evolution of black clouds of carbon, when added to concentrated nitric acid in a basin.

(iv) It readily decomposes on heating, yielding water, brown vapours of nitrogen dioxide and oxygen : $4HNO_3=2H_2O+4NO_2+O_2$.

(v) It is a *powerful oxidising agent.*—Ready liberation of oxygen from nitric acid makes it a powerful oxidising agent, particularly when hot and concentrated. (a) Hot concentrated acid oxidises sulphur to sulphuric acid, iodine to iodic acid, and phosphorus to phosphoric acid. $S+2HNO_3=H_2SO_4+2NO$; $3I_2+10HNO_3=6HIO_3+10NO+2H_2O$.

$$4P+10HNO_3+H_2O = 4H_3PO_4+5NO+5NO_2.$$

(b) Glowing charcoal burns brilliantly in strong acid ; warmed saw-dust bursts into flame in the acid :

$$C + 4HNO_3 = CO_2 + 4NO_2 + 2H_2O.$$

Some saw-dust is heated on a sand bath in a basin until it begins to char ; it inflames on pouring on it a few drops of *fuming nitric acid* very carefully from a test tube. Yellow-coloured **fuming nitric acid** containing dissolved oxides of nitrogen, is a powerful oxidising agent, and is made by distilling concentrated nitric acid with a little starch, which reduces some nitric acid to the nitrogen oxides NO and NO_2.

(c) Concentrated nitric acid oxidises ferrous salts to ferric salts—the reaction is quantitative. Thus the acid converts ferrous sulphate in presence of sulphuric acid to ferric sulphate :

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

(d) Hot dilute or cold concentrated acid liberates sulphur from hydrogen sulphide and iodine from potassium iodide :

$$3H_2S + 2HNO_3 = 3S + 2NO + 4H_2O.$$

$$6KI + 8HNO_3 = 3I_2 + 6KNO_3 + 2NO + 4H_2O.$$

Sulphur dioxide is oxidised to sulphuric acid by nitric acid :

$$2HNO_3 + SO_2 = H_2SO_4 + 2NO_2.$$

(e) Hot concentrated nitric acid reacts with concentrated hydrochloric acid, yielding chlorine, nitrosyl chloride and water :

$$3HCl + HNO_3 = Cl_2 + NOCl + 2H_2O.$$

A mixture of concentrated nitric acid (1 vol.) and hydrochloric acid (3 vols.) is known as **aqua regia** : it dissolves gold and platinum.

$$Au + 4HCl + HNO_3 = HAuCl_4 + NO + 2H_2O.$$

(vi) **Reactions with metals.**—Nitric acid reacts with all metals except gold, platinum, tantalum, rhodium and iridium : iron and chromium become '*passive*' in the concentrated acid : *aluminium is scarcely attacked by cold nitric acid.* Tin and antimony are converted into their oxides. The remaining metals yield nitrates. Since in its action upon metals, nitric acid acts both as *an acid and an oxidising agent*, the attack on the metal is always (except in the case of very dilute acid and magnesium or manganese) accompanied by reduction of the nitric acid to oxides of nitrogen, nitrogen, or ammonia, etc.—the nature of the product depending upon (a) *strength of the acid*, (b) *temperature*, (c) *nature of the metal*, and (d) *products of reaction in the solution*. *Hydrogen* is evolved only by magnesium or manganese, acting upon very dilute (1 or 2 per cent) and cold nitric acid :

$$Mg + 2HNO_3 = Mg(NO_3)_2 + H_2.$$

The mechanism of reduction of nitric acid by metals may be explained by assuming that the initial attack of metals on nitric acid liberates nascent hydrogen which then reduces the excess of nitric acid. The theory explains the action of such metals as iron and zinc which are more electro-positive than hydrogen. The action of zinc upon strong nitric acid, yielding nitrogen dioxide may be explained as follows :

$$\begin{aligned} Zn + 2HNO_3 &= Zn(NO_3)_2 + 2H \\ 2HNO_3 &= H_2O + 2NO_2 + O \\ 2H + O &= H_2O \\ \hline Zn + 4HNO_3 &= Zn(NO_3)_2 + 2H_2O + 2NO_2 \end{aligned}$$

But the metals such as copper, silver and mercury are less electro-positive than hydrogen. It is, therefore, suggested that the initial step in the attack is the oxidation of the metal to its oxide which then dissolves in the acid.

$$\begin{aligned} 3Cu + 2HNO_3 &= H_2O + 2NO + 3CuO. \\ 3CuO + 6HNO_3 &= 3H_2O + 3Cu(NO_3)_2. \\ 3Cu + 8HNO_3 &= 3Cu(NO_3)_2 + 2NO + 4H_2O. \end{aligned}$$

Action of nitric acid upon few representative metals—different oxides of nitrogen or ammonium nitrate are formed, depending mainly on strength of acid :

Copper :
(i) Hot concentrated $Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2$.
(ii) Cold dilute (1:1) $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$.
(iii) Cold dilute $4Cu + 10HNO_3 = 4Cu(NO_3)_2 + 5H_2O + N_2O$

Zinc :
(i) Hot concentrate $Zn + 4HNO_3 = Zn(NO_3)_2 + 2H_2O + 2NO_2$
(ii) Cold dilute $3Zn + 8HNO_3 = 3Zn(NO_3)_2 + 4H_2O + 2NO$
(iii) Cold very dilute $4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3$.
$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 5H_2O + N_2O$.

Zinc dissolves in dilute nitric acid to form ammonium nitrate—some nitrous oxide and nitric oxide are also evolved.

Iron :
(i) Fairly concentrated or hot dilute $Fe + 4HNO_3 = Fe(NO_3)_3 + 2H_2O + NO$
(ii) Cold dilute $4Fe + 10HNO_3 = 4Fe(NO_3)_2 + 3H_2O + NH_4NO_3$
(iii) Concentrated or fuming acid does not dissolve iron but renders it *passive*.

Mercury :
(i) Hot concentrated $Hg + 4HNO_3 = Hg(NO_3)_2 + 2H_2O + 2NO_2$
(ii) Cold dilute $6Hg + 8HNO_3 = 3Hg_2(NO_3)_2 + 4H_2O + 2NO$

Tin :
(i) Cold dilute $4Sn + 10HNO_3 = 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3$
(ii) Hot concentrated acid produces stannic nitrate, which is readily hydrolysed to a white precipitate of metastannic acid, $H_2Sn_5O_{11}, 4H_2O$, the latter decomposing by heat into tindioxide and water.
$5Sn + 20HNO_3 = H_2Sn_5O_{11}.4H_2O + 5H_2O + 20NO_2$.

Silver : (i) Hot dilute $Ag + 2HNO_3 = AgNO_3 + H_2O + NO$.

Action of HNO_3 on metals : A review of the reduction products of nitric acid and the metallic nitrates formed :

Strength of acid :	Concentrated	Moderately strong (1 acid : 1 water)	Dilute
Copper	NO_2	NO	N_2O
Zinc	NO_2	NO	N_2O & NH_4NO_3
Mercury	NO_2 & $Hg(NO_3)_2$	NO & $Hg_2(NO_3)_2$	—
Tin	NO_2 & metastannic acid	—	NH_4NO_3 & $Sn(NO_3)_2$
Iron	passive	NO & $Fe(NO_3)_3$	NH_4NO_3 & $Fe(NO_3)_2$

Action of Nitric Acid upon Alloys.—Alloys contain two or more metals together, which are separately acted on by the acid. *Brass* (Cu and zinc) and *silver coin* (Ag and Cu) readily dissolve in the concentrated nitric acid. *Bronze* (Cu and Sn), when similarly treated, copper alone dissolves—tin is oxidised to metastannic acid which forms a white precipitate. *Gold coin* (Au + Cu or Ag) containing not more than one-third of gold is only attacked by the hot conc. HNO_3—copper or silver dissolves, gold is left unacted upon.

Tests for Nitric Acid and Nitrates.—(*i*) Reddish brown fumes of nitrogen dioxide are evolved when nitric acid or a nitrate is warmed with concentrated sulphuric acid and copper turnings. Copper dissolves in nitric acid, giving a bluish-green solution.

(*ii*) Rose-red colour is produced on adding a nitrate or nitric acid to a solution of brucine in concentrated sulphuric acid.

(*iii*) **The brown ring test** for nitrate and nitric acid. An excess of freshly prepared solution of ferrous sulphate is added to a cold dilute solution of a nitrate in a test tube, and concentrated sulphuric acid is carefully poured into the liquid so as to form a heavy bottom layer ; a brown ring is formed at the junction of the two liquids. *Nitrites interfere with ring test.*

The ferrous sulphate reduces the nitric acid to nitric oxide NO, which reacts with excess of ferrous sulphate, yielding the brown nitroso compound $(Fe.NO)SO_4$, which appears as a brown ring at the junction of the liquids. The nitroso compound is unstable and decomposes on warming into nitric oxide and the ferrous salt, and consequently while performing the ring test, the test tube is cooled under the tap during the addition of sulphuric acid.

$$2HNO_3 + 3H_2SO_4 + 6FeSO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$
$$FeSO_4 + NO \leftrightharpoons (Fe.NO)SO_4$$

A nitrate (also a nitrite) is *quantitatively* converted to ammonia by heating with zinc and strong caustic soda solution. Aluminium may be used instead of zinc, but Devarda's alloy containing aluminium, copper and zinc is the best. The method is employed for the estimation of nitrites or nitrates, the ammonia being distilled into a measured excess of standard acid. The excess sulphuric acid is then back-titrated against standard alkali.

$$NaNO_3 + 4Zn + 7NaOH = NH_3 + 4Na_2ZnO_2 + 2H_2O.$$

In presence of sulphuric acid mercury reduces nitric acid quantitatively to nitric oxide : $6Hg + 3H_2SO_4 + 2HNO_3 = 3Hg_2SO_4 + 4H_2O + 2NO$.

The reaction is used to estimate nitric acid in Lunge's nitrometer—a measured volume of the nitrate solution is shaken with concentrated H_2SO_4 and mercury and the volume of NO formed is measured.

Nitric Acid contains Hydrogen, Oxygen and Nitrogen.—(i) As already stated (p. 179) when strong nitric acid is allowed to drop on red-hot pumice stone, it decomposes into oxygen, nitrogen dioxide and water vapours—the gas mixture is led through ; (a) a U-tube (kept in cold water) in which drops of liquid collect—the liquid is recognised to be water by the blue colour it gives with anhydrous copper sulphate, and hence the presence of hydrogen in nitric acid, and then (b) a second U-tube (cooled in freezing mixture) in which nitrogen peroxide condenses and oxygen passes on ; a glowing chip bursts into flame in the gas that passes on, and hence it is oxygen. $4HNO_3 = 2H_2O + 4NO_2 + O_2$.

(ii) Moderately strong nitric acid dissolves copper, evolving nitric oxide.

The nitric oxide is passed over copper heated to bright redness in a tube when copper oxide is formed and nitrogen passes on :

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO \; ; \; 2NO + 2Cu = 2CuO + N_2.$$

Uses of Nitric Acid.—Besides its uses in the laboratory nitric acid finds applications : (i) in the production of explosives such as dynamite, gun cotton, nitro-glycerine, picric acid, trinitrotoluene (T.N.T.), and ammonium nitrate. Nitre is a constituent of gunpowder.

(ii) in the manufacture of sulphuric acid, coal tar colours, nitrates and fertilisers.

(iii) in etching designs on wares of brass and bronze, and staining silk, wool, etc., yellow ; in the 'picking' of metals before electro-plating ; in the separation of gold and silver.

(iv) in the manufacture of celluloid, collodion, cellophane, rayon, lacquers and other nitrocellulose products.

Nitrosyl Chloride, NOCl, the chloride of nitrous acid, may be prepared by warming nitroso sulphuric acid with sodium chloride :

$$SO_2(OH).O.NO + NaCl = SO_2(OH)ONa + NOCl.$$

It is an orange-yellow gas with a suffocating odour, easily condenses to a red liquid in a freezing mixture.

It is also formed by direct union of nitric oxide and chlorine :

$$2NO + Cl_2 = 2NOCl.$$ It is present in *aqua regia :*

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

That it is the chloride of nitrous acid is shown by its manner of decomposition by water : $NOCl + H.OH = NO.OH$ (nitrous acid) $+ HCl$.

It is also decomposed by alkali in the normal manner :

$$NOCl + 2KOH = KNO_2 + KCl + H_2O.$$

It is without any action on gold or platinum, but attacks mercury :

$$2NOCl + 2Hg = Hg_2Cl_2 + 2NO,$$ and most other metals.

Manufacture of nitric acid.—(i) *Distillation of sodium nitrate with concentrated sulphuric acid.*—Chile salt petre and concentrated sulphuric acid (in 3 : 2 molecular proportions) are placed in a large cast-iron retort which is connected by water-cooled earthenware or silica pipes to a series of stoneware bottle, and then with a tower, filled with stoneware balls, down which water is sprayed (fig. 98). The retort is set in a brick work furnace, and is carefully heated by coke fires to about 200-250°C. The vapours of nitric acid which is evolved according to the equation,

$$3NaNO_3 + 2H_2SO_4 = Na_2SO_4 + NaHSO_4 + 3HNO_3$$

are cooled by passing through the silica spirals cooled in water and are condensed in the stone-ware bottles as concentrated nitric acid. Any uncondensed vapour which is largely nitrogen peroxide (from the decomposition of nitric acid), is absorbed by water in the tower yielding weak nitric acid :

$$4NO_2 + O_2 + 2H_2O = 4HNO_3.$$

The residue in the retort which is a mixture of sodium sulphate and bisulphate is tapped out in the liquid state through an exit at the bottom of the retort. When solid, it is known as **nitre-cake.** The acid is of 90—95 per cent strength. It may be concentrated to 98 per cent by distillation with strong sulphuric acid.

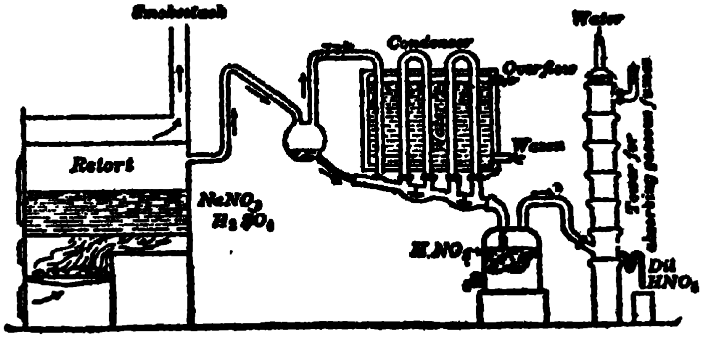


Fig. 98

Nitric acid *vapour* does not corrode iron, which is attacked by the liquid acid. The method,—though easy to carry out and largely used in India, is based on *imported* Chile salt petre.

(ii) **The catalytic oxidation of ammonia : Ostwald process.**—In this process ammonia is oxidised to nitric oxide by the oxygen of air in presence of heated *platinum gauze catalyst*—more than 90% of NH_3 is converted into NO :

$$4NH_3 + 5O_2 = 4NO + 6H_2O + 305,000 \text{ calories.}$$

An excess of air over that required theoretically to form nitric oxide is necessary. The air is preheated to about 500°C in a heat exchanger (2), by the hot gases produced by the oxidation of ammonia, and then

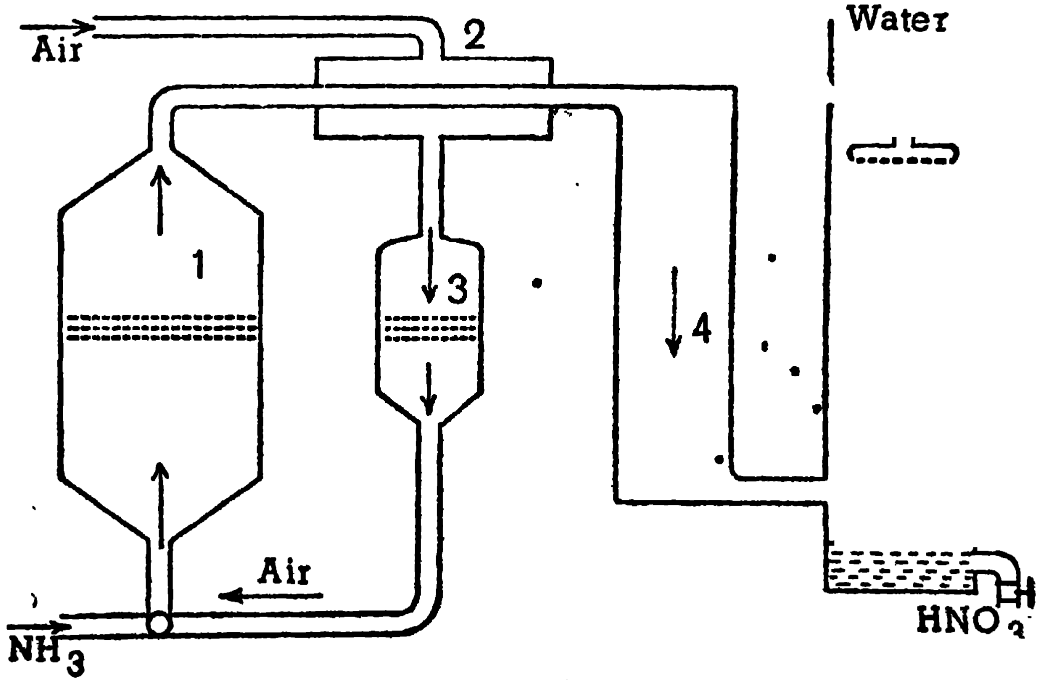


Fig. 99

freed from dust particles by filtration through woollen cloth in the air filter (3). A mixture of pure and dry ammonia (usually the synthetic ammonia from the Haber plant) and the preheated air in the

UTTARPARA

proportion of 1:7.5 by volume is *rapidly* (time of contact with catalyst is about 1/1000 second ; otherwise ammonia is oxidised to nitrogen) passed through a layer of fine-mesh *platinum gauze catalyst* stretched across an aluminium box (1) (fig. 99) called a converter—the catalyst is initially brought to the reaction temperature of 750°—900°C by electrical heating ; once started the *exothermic reaction* proceeds automatically. The hot products of the reaction in passing through the heat-interchanger heats the incoming air and so the process continues without external heating.

The somewhat cooled products of the reaction which contain nitric oxide, some nitrogen, excess air and steam, after leaving the heat-interchanger (2), are cooled to about 50°C in an aluminium pipe (4) where the nitric oxide is oxidised to nitrogen dioxide by the oxygen of the accompanying excess air. $2NO + O_2 = 2NO_2$. The nitrogen dioxide is then absorbed in water in several stainless steel towers (5) packed with broken quartz to form nitric acid.

$$2NO_2 + H_2O = HNO_3 + HNO_2 \; ; \qquad 3HNO_2 = HNO_3 + 2NO + H_2O$$

The nitric oxide liberated is reoxidised by the air present, forming NO_2 which re-enters the reaction. $2NO + O_2 = 2NO_2$. A 50% solution of nitric acid is collected from the bottom of the tower.

When the gases become very dilute, oxidation of NO is very slow, and the exit gases from the last absorption tower contain NO and NO_2 mainly, which are absorbed in NaOH or Na_2CO_3 solution, producing sodium nitrite :

$$NO + NO_2 \leftrightharpoons N_2O_3.$$
$$N_2O_3 + Na_2CO_3 = 2NaNO_2 + CO_2$$

Ostwald method is the chief process of making nitric acid—yield is 90 per cent. Modern plants operate at a pressure of 7 to 8 atmospheres, yielding 60 per cent acid. Platinum-rhodium gauze or a mixture of Fe_2O_3 and Bi_2O_3 also acts as a catalyst for this process.

The dilute acid may be concentrated by distillation until the liquid attains the composition of constant boiling point containing 68% HNO_3 (boiling point 121°) ; this is the ordinary commercial acid of density 1.414. It may be concentrated to 98% by distillation with concentrated sulphuric acid.

(iii) **From the air : Birkeland-Eyde process.**—Nitric oxide is formed by electric discharges in air—the oxidation is in *endothermic reaction :*

$$N_2 + O_2 \rightleftharpoons 2NO - 2 \times 21{,}600 \text{ calories.}$$

The proportion of NO at equilibrium, therefore, increases with rising temperature :

Temperature °C	1538	1604	1760	2307	2402	2927
% NO by volume	0.07	0.42	0.64	2.05	2.23	5

The yield of NO is greater, the higher the temperature. Consequently, to secure the maximum yield, technically air is heated to a high temperature of 3000°C in an electric arc flame, but if the gases be then cooled slowly, the percentage of NO gradually decreases corresponding to lower temperature. In order to avoid this subsequent decomposition of NO, the gases are swept away from the flame and cooled quickly, i.e., the high temperature equilibrium mixture is suddenly 'chilled' or 'frozen', to 1000°C, below which temperature the rate of decomposition of NO is very slow.

Air is drawn through an electric arc set up between water-cooled copper electrodes—the arc is spread out by an electromagnet into a disc of flame the temperature of which is about 3000°C (fig. 100). Nitric oxide is produced at the higher temperature of the flame where the equilibrium $N_2 + O_2 \rightleftharpoons 2NO$ is set up. The gases issuing from the arc is quickly cooled to about 1000°C to stabilise the nitric oxide—the yiled is only 1 per cent by volume. The gases are then gradually

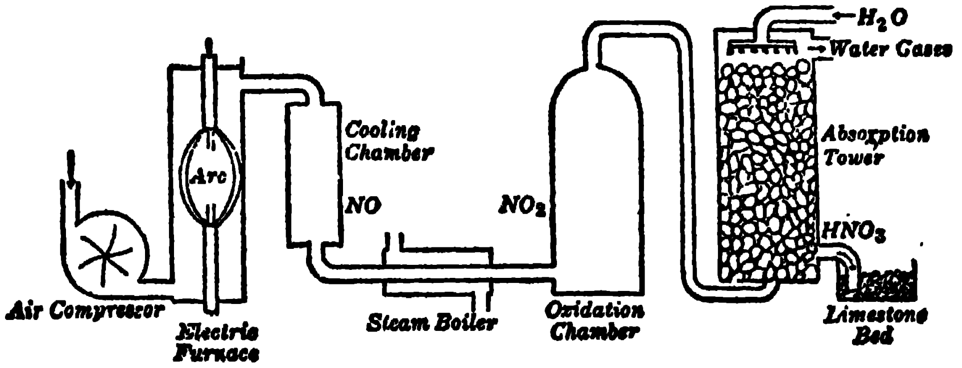


Fig. 100

cooled when the nitric oxide is oxidised to nitrogen peroxide, which is absorbed by water, giving nitric acid.

$$2NO + O_2 = 2NO_2\ ;\quad 3NO_2 + H_2O = 2HNO_3 + NO.$$

This method, at one time the chief process of fixing atmospheric nitrogen, was carried out in Norway in 1902, utilising hydro-electric power, but is obsolete nowadays due to high power costs and it has been replaced by ammonia synthesis and oxidation of ammonia to nitric acid.

Distinction between Nitrites and Nitrates.—For wet tests aqueous solutions of $NaNO_3$ and $NaNO_2$ are used.

Dry tests	Nitrate	Nitrite
(i) Action of heat	Nitrates decompose, $NaNO_3$ and KNO_3 yielding nitrite and O_2, and heavy metal nitrates, e.g., $Pb(NO_3)_2$, evolving reddish brown fumes	Nitrites except $NaNO_2$ and KNO_2, decompose, evolving reddish brown fumes.
(ii) Dilute H_2SO_4	No action	Reddish-brown fumes
(iii) Concentrated sulphuric acid	Pungent acid fumes, coloured brown by NO_2, on heating ; colour deepens on addition of copper-turnings	Reddish-brown fumes
Wet tests		
(iv) KI solution + dilute H_2SO_4 + starch solution	No action	Blue colour
(v) $KMnO_4$ solution + dilute H_2SO_4	No action	Pink colour is discharged
(vi) Metaphenylene-diamine + HCl	No action	Brown colour
(vii) Sulphanilic acid + α-naphthylamine + acetic acid	No action	Pink colour
(viii) Brucine + concentracted H_2SO_4	Rose-red colour	No action
(ix) Zinc dust + NaOH ; heat	NH_3 evolved	NH_3 evolved
(x) *Ring test :* $FeSO_4$ solution + H_2SO_4	Brown ring only in presence of conc. H_2SO_4	Brown ring even in presence of dilute H_2SO_4

The nitrate cannot be detected in presence of a nitrite by the ring test, as the latter also gives this test. The nitrite is, therefore, completely decomposed first by boiling with NH_4Cl or a mixture of urea and dilute H_2SO_4, and then the nitrate is tested by the ring test.

Exercises

1. How may nitrogen be obtained from (*a*) air, (*b*) ammonia, (*c*) nitric acid ? Under what conditions does nitrogen combine with (*i*) hydrogen, (*ii*) oxygen, (*iii*) magnesium and (*iv*) calcium carbide ? Describe the action of water on the products formed in each case.

2. How would you prove that air and water contain a common constituent ? What are the evidences to indicate that in one case the common constituent is chemically combined while in the other it merely forms part of a mixture ?

3. What are the chief constituents of air ? Describe Lavoisier's experiment on the composition of air. How is the composition of air affected by plant and animal life ?

4. How would you obtain a specimen of dry ammonia gas ? How and under what conditions does it react with (*i*) lead oxide, (*ii*) chlorine, (*iii*) sodium, (*iv*) carbon dioxide, (*v*) ferric chloride solution, and (*vi*) copper oxide ? *Punjab* '51

5. Give an account of one method of manufacturing ammonia from atmospheric nitrogen. How and under what condition does ammonia react with (*i*) copper sulphate, (*ii*) silver chloride, (*iii*) mercurous chloride, (*iv*) calcium sulphate and carbon dioxide ? *Nagpur Inter.*

6. How has the composition of ammonia been determined volumetrically and gravimetrically ? How may ammonia be converted into (*a*) nitrogen (*b*) nitric acid. How is ammonia detected ? *Calcutta* '44

7. How are the ammonium salts obtained ? Indicate their uses. Describe the action of heat upon the following substances :—(*a*) ammonium chloride, (*b*) ammonium nitrite, (*c*) ammonium nitrate, (*d*) lead nitrate, and (*e*) nitric acid. How are the ammonium salts detected ?

8. Give the names and formulae of 5 oxides of nitrogen. Describe the preparation of a pure sample of nitrous oxide. How would you remove a trace of nitric oxide from nitrous oxide ? In what respects does nitrous oxide differ from oxygen ? How has its formula been arrived at ?

9. How would you prepare nitric oxide in the laboratory ? How has the composition of the gas been determined ? What happens when the gas is slowly passed for some time into a jar of air confined over water ? How would you qualitatively distinguish between oxygen, nitrous oxide and nitric oxide ?

10. How is nitric acid prepared in the laboratory ? How may the nitrogen present in nitric acid be converted into (*i*) ammonia, (*ii*) nitrous oxide, (*iii*) nitric oxide, and (*iv*) free nitrogen ? How would you prove that nitric acid contains nitrogen, hydrogen and oxygen ?

11. How is nitric acid manufactured from atmospheric nitrogen ? How and under what conditions does nitric acid react with (*i*) charcoal, (*ii*) *iodine*, (*iii*) brass, (*iv*) iron and (*v*) silver coin ? *Madras* '49

12. How would you prepare from sodium nitrate (*i*) concentrate nitric acid, (*ii*) nitrous acid ? Compare their actions when treated with (*a*) ferrous sulphate, (*b*) potassium iodide, (*c*) hydrogen sulphide.

13. Describe experiments by which you can prove that both air and nitrous oxide contain the same constituents. What is the evidence that in one case the constituents are chemically combined, while in the other they merely from a mechanical mixture ? *Calcutta Inter.* '50

14. Explain what happens when :

(*i*) glowing charcoal is dropped into concentrated nitric acid ;

(ii) a mixture of air and ammonia is passed over heated platinum gauze ;

(iii) strong sulphuric acid is poured carefully into ferrous sulphate dissolved in cold dilute nitric acid ;

(iv) ammonia is passed over heated sodium, and the product that is formed, is then treated with water ;

(v) nitrogen is passed over heated aluminium, and the resulting product is then warmed with dilute caustic soda ;

(vi) a mixture of nitric oxide and hydrogen is passed over heated platinum ;

(vii) carbon dioxide is led into a suspension of calcium sulphate in ammonium hydroxide ;

(viii) nitrogen is passed over heated calcium carbide, and the product that results is then treated with steam ;

(ix) air is led into a tube containing red-hot copper followed by magnesium heated to redness in a furnace ;

(x) ammonium hydrate is gradually added in excess to a solution of copper sulphate.

15. State what you would observe and what gases are produced, when ammonium nitrate and lead nitrate are separately heated.

Supposing 17 gm. of sodium nitrate are completely converted into nitric acid, what weight of the latter would be produced ? *Ans.* 12.6

16. Explain what happens when :

(i) a gas obtained by heating manganese dioxide with strong hydrochloric acid, is led into a flask containing ammonium hydroxide ;
(ii) sodium nitrate solution is heated with zinc dust and caustic soda, and the evolved gas is led into sulphuric acid.
(iii) a thin paste of bleaching powder is run into ammonium hydroxide in a flask ;
(iv) a mixture of potassium nitrate, ferrous sulphate and dilute sulphuric acid is heated in a flask ;
(v) nitre is fused with lead ;
(vi) a copper coin is dropped into strong nitric acid in a test tube ;
(vii) a mixture of nitrous and nitric oxides is led into a cold saturated solution of ferrous sulphate ;
(viii) a gas obtained by heating ammonium nitrite is led into a tube containing red-hot magnesium ;
(ix) hydrogen sulphide is passed into strong nitric acid ;
(x) starch is added to a mixture of potassium nitrite and potassium iodide acidified with dilute sulphuric acid.

17. Describe the preparation and collection of nitric oxide in the laboratory. How would you show that nitrogen and oxygen are contained in nitric oxide ?

Expalin why a glowing chip is extinguished in nitric oxide, but burning magnesium continues to burn.

What volume of nitric oxide at N.T.P. can be produced by the action of nitric acid on 12.7 gm. of copper ? (at. wt. of Cu = 63.5). *Ans.* 2.99 litres.

18. You are given three cylinders containing nitrous oxide, nitric oxide and air respectively. Describe experiments by which you can distinguish between them. How can nitric oxide be converted into nitric acid and the latter back again into nitric oxide ? Give equations. Describe what happens when nitric oxide is passed into a solution of ferrous sulphate. *Calcutta* 1950

XXI

THE HALOGENS

The elements fluorine, chlorine, bromine and iodine are called *halogens*, or 'salt-forming' elements (*hals* means sea-salt), as the last three are contained in sea-water, and their sodium salts resemble the sea-salt, sodium chloride.

Fluorine

Formula F_2. Atomic weight 19.00. Atomic number 9. Valency 1. Boiling point—187°C. Freezing point—233°C. Density at the b. pt. 1.108.

Occurrence.—The most important minerals of fluorine are : *fluorspar*, CaF_2, and *cryolite* AlF_3, 3NaF, the latter being found in Greenland only. *Fluor-apatite*, CaF_2, $3Ca_3(PO_4)_2$, is another mineral containing fluorine. The enamel of teeth contains about 0.3 per cent of fluorine.

Isolation of Fluorine.—Hydrofluoric acid, obtained by heating fluorspar with strong sulphuric acid by Scheele in 1771, was known as an agent for etching glass ever since. It was observed by Davy in 1813 that the hydrofluoric acid was analoguous to hydrochloric acid, and was made up of hydrogen and an *yet undiscovered element*, similar to chlorine, which he named *fluorine*. But all attempts towards its isolation by Davy, Fremy, Gore and others were uniformly fruitless. The element was not actually isolated until 1886, since the method of obtaining chlorine was not available for its isolation. The difficulties were :

(i) An aqueous solution of hydrofluoric acid on electrolysis gave only ozonised oxygen and hydrogen—no fluorine was obtained, since the liberated fluorine attacked water : $2H_2O + 2F_2 = 4HF + O_2$; $3H_2O + 3F_2 = 6HF + O_3$.

The anhydrous hydrofluoric acid, on the other hand, *is a non-conductor of electric current.*

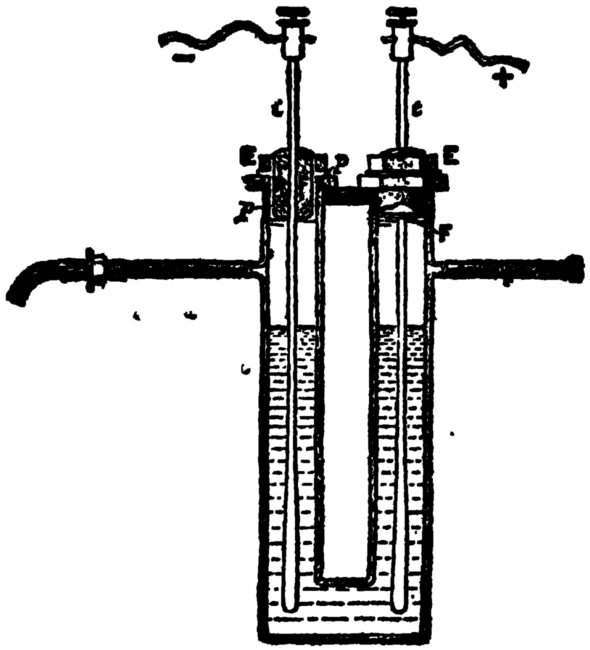


Fig. 101

(ii) It was difficult to obtain an electrolytic vessel of suitable material, since fluorine was a highly reactive element and attacked such materials as carbon, platinum and glass from which the chemical apparatuses were generally made,

(iii) Fluorine and hydrofluoric acid are highly poisonous ; and lastly,

(iv) Hydrofluoric acid is highly *volatile*, its boiling point being only 19.5°C ; consequently, low temperature was necessary for the electrolysis. Want of a suitable refrigerant was also partially responsible for the failure of the earlier attempts to isolate the fluorine. Moissan got over these difficulties, and was successful in isolating fluorine in 1886.

In 1869 Gore noticed that *anhydrous* hydrofluoric acid conducts electric current *when potassium hydrogen fluoride* was dissolved in it. By electrolysing this solution in a vessel of *platinum-iridium alloy* (which is resistant to corrosion by fluorine) with electrodes of the same metal, Moissan isolated fluorine in 1886.

The solution was cooled to −23°C, using a bath of boiling methyl chloride which boil at −23°, at which temperature the hydrofluoric acid remained in the liquid state.

The electrolysis was carried out in a U-tube (fig. 101 & 102) made of *platinum-iridium alloy ;* the electrodes of the same alloy, and thickened at the ends, were insulated from the U-tube by means of fluorspar stoppers covered outside with shellac. The apparatus was provided with two side tubes for leading out the gases liberated at the electrodes. The electrolyte, i.e., *the solution of potassium hydrogen fluoride in anhydrous liquid hydrofluoric acid,* was contained in the U-tube which was immersed in a bath of boiling methyl chloride, b.p.—23°C, constantly renewed, and a potential was applied.

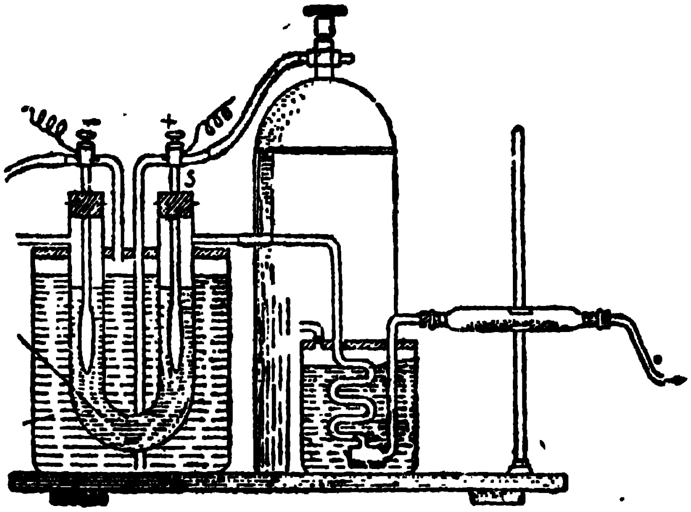


Fig. 102

During electrolysis hydrogen was evolved at the cathode and fluorine at the anode. The fluorine was led through a spiral of platinum, also cooled in methyl chloride, to condense the accompanying vapours of hydrofluoric acid, and then through a tube of the same metal packed with *fused sodium fluoride* to remove the last trace of hydrofluoric acid vapours, forming sodium hydrogen fluoride, $NaF + HF = NaHF_2$. The gas was then collected in a platinum jar by the upward displacement of air.

The electrolyte is the potassium fluoride, the acid acting as an ionising solvent only : $KHF_2 = KF + HF$; $KF \rightleftharpoons K^+ + F'$.

At anode $F' - e = F$; $F + F = F_2$.
At cathode. $K^+ + e = K$; $2HF + 2K = 2KF + H_2$.

The potassium reacts with hydrofluoric acid, liberating hydrogen and forming potassium fluoride which again undergoes electrolysis.

The gas evolved at anode was absorbed in iron wire in a weighed platinum tube by Moissan who found that for every gram of hydrogen liberated at cathode the iron wire gained in weight by 19 gms ; the gas was thus concluded to be free fluorine.

Preparation.—Fluorine attacks water and hence cannot be prepared by the electrolysis of an aqueous solution of hydrofluoric acid or a fluoride :

$$2F_2 + 2H_2O = 4HF + O_2.$$

(i) Fluorine is prepared nowadays by the electrolysis of *fused* potassium hydrogen fluoride, m.p. 230°C, in an electrically heated U-shaped copper vessel (fig. 103) fitted with graphite electrodes through bakelite stoppers—the copper is coated with a protecting film of copper fluoride initially formed. The fluorine evolved from the anode is led through two copper U-tubes packed with dry sodium fluoride to remove the hydrofluoric acid vapours. Hydrogen is evolved from the cathode.

Since the isolation of fluorine eluded the chemists for over a century, it long remained a mere chemical curiosity ; but fluorine is now easily available and is handled almost as readily as chlorine. Sulphur hexafluoride is an effective insulator in high voltage apparatus. Uranium hexafluoride finds application in the separation of uranium isotopes. *Freon*, CF_2Cl_2, is a refrigerant. Fluroine also finds use in making insecticides.

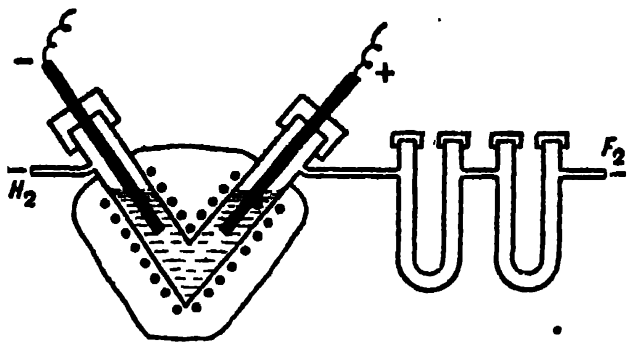


Fig. 103

(ii) Fluorine is now made on a large scale by the electrolysis of a fused mixture of potassium hydrogen fluoride with 1% lithium fluoride in a jacketted steel tank with a carbon anode and a steel cathode—the products of electrolysis are prevented from mixing by means of a fine mesh metal screen under the electrolyte. The temperature of the bath is kept at about 100°C by circulating hot water through the outside jacket.

Properties.—(i) Fluorine is a *pale greenish yellow, poisonous gas* of penetrating smell like that of hypochlorous acid, and having no marked action on dry glass below 100°, may be kept in glass vessels.

(ii) It is the most chemically active of all elements. It combines directly with nearly all metals—*sodium, potassium, etc., catch fire in the gas*, yielding their fluorides. *It does not directly combine with oxygen or nitrogen*, but other non-metals such as sulphur, phosphorus, charcoal, bromine and iodine, etc. burn spontaneously in the gas.

$$C + 2F_2 = CF_4 \; ; \; 2B + 3F_2 = 2BF_3.$$

Boron

(iii) It has a great affinity for hydrogen ; a jet of hydrogen inflames in a jar of fluorine, forming hydrogen fluoride. It combines explosively with hydrogen even at —252°. Moist fluorine and hydrogen explode in the dark. It decomposes water liberating ozonised oxygen.

$$2H_2O + 2F_2 = 4HF + O_2 \; ; \quad 3H_2O + 3F_2 = 6HF + O_3.$$

(iv) It displaces chlorine, bromine, or iodine, from the corresponding hydracid and its salt ; thus it liberates chlorine from potassium chloride : $2KCl + F_2 = 2KF + Cl_2$.

(v) It reacts with cold dilute alkali, forming fluorine monoxide and no oxyacids, but oxygen is evolved with concentrated alkali :

$$2NaOH+2F_2 = F_2O+2NaF+H_2O \; ; \quad 4NaOH+2F_2 = 2H_2O+4NaF+O_2.$$

(vi) *Fluorine is an intense oxidising agent* ; thus it oxidises potassium chlorate, $KClO_3$, to potasium perchlorate, $KClO_4$.

Hydrofluoric acid, HF.—Preparation.—An aqueous solution of hydrofluoric acid is prepared by distilling a mixture of powdered fluorspar and strong (90 per cent) sulphuric acid in a lead retort—the mixture being carefully heated below 300° (m.p. of lead 327°) on a sand bath. The vapours of hydrofluoric acid evolved are absorbed in water contained in a lead receiver (fig. 104). The solution may be kept in bottles of wax or gutta-percha :

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

Anhydrous hydrofluoric acid is obtained by heating dry potassium hydrogen fluoride, KHF_2, called **Fremy's salt.** Dry potassium hydrogen fluoride is heated in a platinum or copper retort connected with a receiver of the same metal, immersed in a freezing mixture of ice and common salt. The double fluoride decomposes by heat into potassium fluoride and hydrofluoric acid gas :

$$KHF_2 = KF + HF.$$

The hydrofluoric acid gas condenses to a colourless liquid in the anhydrous state in the receiver.

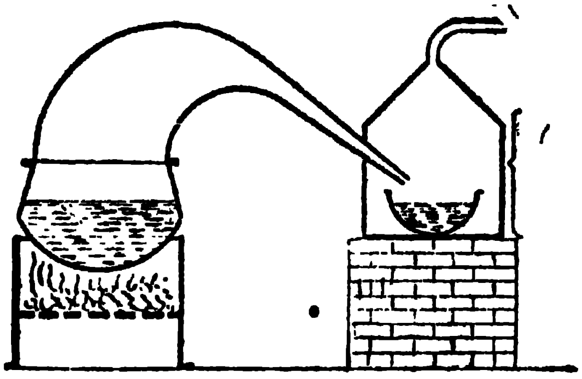


Fig. 104

Traces of moisture that may yet remain are removed from hydrofluoric acid by electrolysis with platinum electrodes ; the acid becomes non-conducting when all the water is removed. Anhydrous hydrofluoric acid is thus obtained :

The **Fremy's salt,** KHF_2, is prepared as follows : An aqueous solution of hydrofluoric acid is divided into two equal parts—one part is neutralised gradually with potassium carbonate until evolution of carbon dioxide ceases, potassium fluoride being formed. The neutralised solution is then mixed with the other half of the acid, and the solution evaporated to dryness. It is then dried at 100°C, and then exposed in a vacuum desiccator over concentrated sulphuric acid to remove the last trace of moisture. Fremy's salt melts at 230° and decomposes at higher temperature :

$$2HF + K_2CO_3 = 2KF + H_2O + CO_2 \;;\quad KF + HF \rightleftharpoons KHF_2.$$

Properties.—(i) Hydrofluoric acid is a *highly poisonous, colourless,* strongly fuming *liquid* of boiling point 19.5° only. HF and its vapours are highly corrosive poisons ; they violently attack the skin, forming sores.

The sores are immediately treated with magnesium hydroxide. Hydrofluoric acid causes permanent loss of voice on inhalation and finally death. Rubber gloves are used in working with the acid.

(ii) It is completely miscible with water—the aqueous solution is conducting ; *the anhydrous acid is a non-electrolyte.*

The aqueous solution behaves as a *weak acid,* and attacks all but noble metals, yielding metallic fluorides and hydrogen. Sodium and potassium fluorides readily combine with hydrogen fluoride to form acid fluorides :

$$Fe + 2HF = FeF_2 + H_2 \;;\quad HF + NaF = NaHF_2.$$

(iii) The acid is *associated* at low temperature—its vapour at 15° to 19° is a mixture of HF and H_6F_6. It is H_2F_2 in concentrated solution. The vapour density at 100°C agrees with the formula HF.

Its composition was determined by Gore by heating silver fluoride at 100° in hydrogen in a platinum vessel—twice the volume of hydrogen fluoride gas was obtained. Hence the formula at 100° is HF :

$$2AgF + H_2 = 2HF + 2Ag.$$

(iv) It is highly corrosive and *attacks glass and porcelain*, and hence kept in gutta-percha or glass vessels coated internally with paraffin.

(v) **Action on silica and etching of glass.**—Hydrofluoric acid attacks glass, forming silicon tetrafluoride and water. The use of HF in etching glass depends upon its action upon the silica in the glass :

$$4HF + SiO_2 = SiF_4 + 2H_2O.$$

A glass plate is coated with wax and the designs which are to be etched are scratched on its surface with a pointed pin to remove wax. The design is then treated with an aqueous solution of hydrofluoric acid by means of a brush when the pattern is readily produced on the glass. The plate is finally washed out with water to remove the excess acid, followed by turpentine to dissolve out the wax.

(vi) Gaseous hydrogen fluoride is absorbed by dry sodium fluoride :

$$HF + NaF = NaHF_2.$$

Tests.—(i) The acid is readily detected by its etching of glass.

(ii) Fluorides are detected by heating them with strong sulphuric acid and *sand* when fumes of silicon tetrafluoride are evolved. Water drops held in the fumes by a glass rod becomes opaque due to deposition of insoluble silicic acid.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF\ ;\quad 2HF + SiO_2 = SiF_4 + 2H_2O\ ;$$
$$3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4 \text{ (silicic acid).}$$

(iii) Soluble fluorides in aqueous solution give a white precipitate with barium chloride, which is soluble in strong hydrochloric acid.

$$2NaF + BaCl_2 = BaF_2 + 2NaCl.$$

Uses.—The hydrofluoric acid is used in etching designs on glass (marks and graduations on glass apparatus), in making artificial cryolite, and removing silica from graphite and sand from iron castings.

(ii) Sodium fluoride is used as an antiseptic in brewing and dyeing industry to prevent the growth of *wild yeasts*.

(iii) Sodium and zinc fluorides are used in the preservation of wood.

(iv) Sodium fluosilicate is an insecticide ; magnesium fluosilicate is a preservative of cement surfaces. Hydrofluoric acid finds use in the analysis of silicate minerals and is a catalyst in many organic reactions.

Fluorides.—Fluorides are analogues to chlorides, but unlike the latter, many of them combine with HF to form acid fluorides : $KF + HF = KHF_2$. Acid ammonium fluoride is obtained by heating ammonium fluoride :

$$2NH_4F = NH_3 + (NH_4)HF_2.$$

Silver fluoride is soluble in water (AgCl, AgBr, and AgI are insoluble), and calcium fluoride is insoluble in water ($CaCl_2$, $CaBr_2$, and CaI_2 are soluble). Fluorine differs from other halogens in forming stable complex acids, e. g., hydrofluoboric acid, HBF_4 and hydrofluosilicic acid, H_2SiF_6.

Chlorine

Formula Cl_2, Valency 1. B. pt.—34.6°. M. pt.—-101.6°. Atomic weight 35.457. Atomic number 17. Solubility, 1 vol. of water dissolves 4.6 volumes at 0°. Liquefaction liquefies at 6 atmospheres at 15°.

History and Occurrence.—The gas was discovered by Scheele in 1774 by heating hydrochloric acid (*muriatic acid*, as it was then called) with manganese dioxide. It was first thought to be an oxide of the acid, and hence called *oxymuriatic* acid, but in 1810 Davy conclusively proved it to be an element and named it *chlorine* because of its greenish yellow colour.

Chlorine does not occur free in nature but is found in large quantities as *common salt* or *rock salt*, NaCl. Besides, it occurs in the Stassfurt deposits in Germany as *sylvine*, KCl, and *carnallite*, KCl, $MgCl_2$, $6H_2O$. It also occurs as *hornsilver*, AgCl.

Laboratory preparation.—Chlorine is usually prepared in the laboratory by the oxidation of hydrochloric acid with (a) *pyrolusite* (mineral form of manganese dioxide, MnO_2), or (b) *potassium permanganate*, $KMnO_4$.

(a) Powdered manganese dioxide (pyrolusite) is taken in a flask fitted with a thistle funnel and a delivery tube (fig. 105). Strong hydrochloric acid is poured down the funnel in quantity ; chlorine is liberated as a greenish yellow gas on gently warming the flask. The gas is bubbled through water in a wash-bottle to dissolve out hydrochloric acid vapours and then through concentrated sulphuric acid to remove moisture. The pure and dry gas is then collected in dry gas jars by the upward displacement of air (it is 2½ times heavier than air). It may also be collected over saturated brine or hot water in which it is much less soluble, but not over water in which it dissolves rather readily, nor over mercury which it attacks :

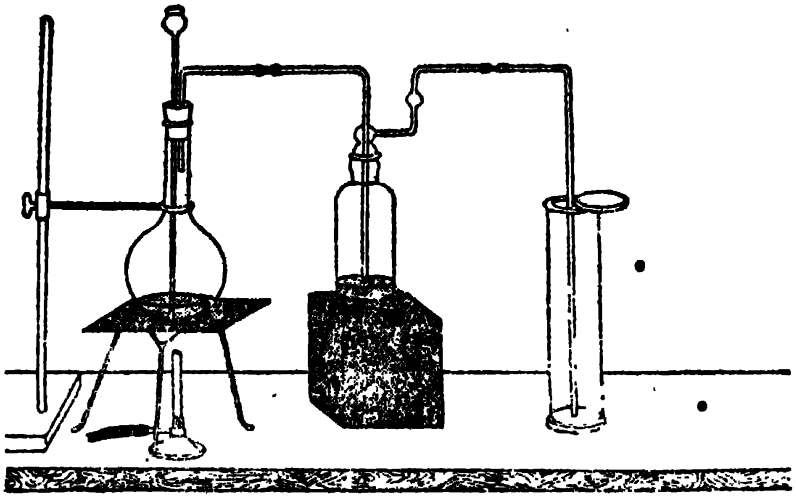


Fig. 105

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The action of manganese dioxide upon hydrochloric acid take place in two steps ; the dark brown solution formed in the cold contains manganese trichloride which decompose on warming with liberation of chlorine :

$$2MnO_2 + 8HCl = 2MnCl_3 + Cl_2 + 4H_2O = 2MnCl_2 + 2Cl_2 + 4H_2O.$$

Instead of hydrochloric acid and manganese dioxide a mixture of *common salt*, 50 per cent *sulphuric acid* and *manganese dioxide* may be heated to prepare chlorine.

$$2NaCl + 2H_2SO_4 = 2NaHSO_4 + 2HCl.$$
$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$
$$2HCl + O = H_2O + Cl_2$$

$$MnO_2 + 2NaCl + 3H_2SO_4 = MnSO_4 + 2NaHSO_4 + Cl_2 + 2H_2O.$$

(b) A convenient supply of chlorine may be obtained by dropping cold concentrated hydrochloric acid upon crystals of potassium permanganate taken in a conical flask. The gas is washed and dired as in method (a). The reaction is :

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

Chlorine is also obtained : (*i*) By the action of dilute acid on bleaching powder.

$$Ca(OC)Cl + 2HCl = CaCl_2 + H_2O + Cl_2.$$

(*ii*) By heating a mixture of potassium dichromate and concentrated hydrochloric acid : $K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$.

(*iii*) By heating platinic chloride or cupric chloride to 600° :

$$PtCl_4 = PtCl_2 + Cl_2 = Pt + 2Cl_2 \,; \quad 2CuCl_2 = Cu_2Cl_2 + Cl_2$$

(*iv*) By the electrolysis of metallic chlorides in aqueous solution or in the fused state. **Pure chlorine** is obtained by the electrolysis of fused silver chloride in a glass U-tube fitted with carbon electrodes.

Properties.—(i) Chlorine is a heavy (about 2½ times as heavy as air) *greenish yellow,* highly poisonous gas with irritating smell and corrosive properties ; it is easily liquefied by cooling and compression.

(ii) It is fairly soluble in water but is very much less soluble than hydrochloric acid, and *hence may be separated from traces of the latter by washing with water.*

(a) The aqueous solution of chlorine, yellowish in colour and smelling strongly of chlorine is known as **chlorine water ;** it contains a mixture of hydrochloric and hypochlorous acid HOCl, the latter liberates nascent oxygen on keeping and particularly *in bright sunlight.* Hence the oxidising and bleaching properties of chlorine water :

$$Cl_2 + H_2O = HCl + HOCl = 2HCl + O.$$

(b) In bright sunlight chlorine directly decomposes water, liberating oxygen ; the reaction is reversible :

$$2H_2O + 2Cl_2 \rightleftharpoons 4HCl + O_2.$$

(c) A saturated solution of chlorine, cooled to 0°, deposits white crystals of *chlorine hydrate,* ~~$Cl_2.8H_2$~~O. $Cl_2 6H_2O$, $Cl_2 8H_2O$ (both are formed)

(iii) It does not burn but *supports combustion* of many elements such as phosphorus, arsenic, antimony, bismuth, sodium and copper.

(*a*) Finely powdered arsenic or antimony, when sprinkled into a jar of chlorine, spontaneously catches fire, yielding a shower of sparks. Pieces of white phosphorus or thin copper foils, on being similarly introduced, ignite spontaneously in the gas.

(*b*) When chlorine is passed over sodium heated in a bulb tube, the metal burns with a bright yellow flame.

$2As + 3Cl_2 = 2AsCl_3$ $\qquad$ $2Na + Cl_2 = 2NaCl$

$Cu + Cl_2 = CuCl_2.$ $\qquad$ $2Sb + 5Cl_2 = 2SbCl_5$

$2P + 5Cl_2 = 2PCl_5$ $\qquad$ $2P + 3Cl_2 = 2PCl_3$

Chlorine directly unites with most metals and many non-metals, yielding chlorides ; but **it is without action upon carbon, nitrogen and oxygen**—their chlorides being prepared indirectly.

(iv) It has great affinity for hydrogen. When exposted to *sunlight* a mixture of hydrogen and chlorine explodes violently to form hydrogen chloride : $H_2 + Cl_2 = 2HCl$.

(*a*) A burning jet of hydrogen continues burning with a greenish flame, when introduced in a jar of chlorine, forming hydrogen chloride (fig. 106). In presence of activated charcoal hydrogen and chlorine readily combine to yield hydrochloric acid—a process of commercial importance.

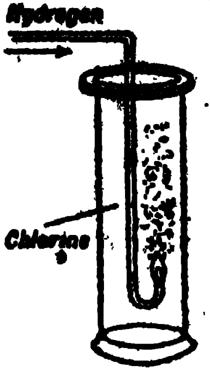


Fig. 106

(*b*) A lighted candle, on being inserted into a jar of chlorine, burns with a small dull-red flame with copious deposition of soot and forming hydrochloric acid.

(c) A piece of paper soaked in turpentine which is a hydrocarbon of the formula $C_{10}H_{16}$, bursts into flame when plunged into chlorine, yielding a cloud of soot mixed with fumes of HCl : $C_{10}H_{16} + 8Cl_2 = 10C + 16HCl$.

In the experiments (b) and (c) chlorine attacks the hydrocarbons (candle is made up of paraffin wax which is a mixture of hydrocarbons), uniting with the hydrogen to form hydrochloric acid and not with carbon which therefore, deposits as soot.

(v) **Action of chlorine on alkalis.**—(a) Chlorine reacts with a *cold alkali* e.g., NaOH, KOH or $Ca(OH)_2$, solution, to give the chloride and **hypochlorite** of the metal *as long as the solution is alkaline.*

$$Cl_2 + H_2O = HCl + HOCl.$$

$$HCl + HOCl + 2NaOH = NaCl + NaOCl + 2H_2O.$$

$$Cl_2 + 2NaOH = NaCl + NaOCl + H_2O.$$

But when all the alkali is removed, i.e., *in presence of excess of chlorine,* the hypochlorite is readily converted into *chlorate.*

Chlorine dissolves in alkaline solution of hydrogen peroxide, giving off oxygen.

$$H_2O_2 + 2NaOH + Cl_2 = 2NaCl + 2H_2O + O_2.$$

(b) *Hot solution of the alkali* also yields chloride and **chlorate** of the metal through the intermediate formation of hypochlorite :

$$3Cl_2 + 6NaOH = 3NaCl + 3NaOCl + 3H_2O.$$

$$\underline{3NaOCl = 2NaCl + NaClO_3.}$$

$$3Cl_2 + 6NaOH = 5NaCl + NaClO_3 + 3H_2O.$$

(c) A solution of calcium hydroxide or milk of lime reacts similarly.

$$2Ca(OH)_2(\text{cold}) + 2Cl_2 = CaCl_2 + Ca(OCl)_2 + 2H_2O.$$

$$6Ca(OH)_2(\text{hot}) + 6Cl_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O.$$

Chlorine reacts with dry slaked lime forming bleaching powder :

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O.$$

Chlorine reacts with calcium oxide at a red heat, yielding calcium chloride and oxygen : $2CaO + 2Cl_2 = CaCl_2 + O_2$.

(vi) **Oxidising action of chlorine.**—It oxidises stannous salts to stannic salts, and ferrous salts to ferric salts :

$$SnCl_2 + Cl_2 = SnCl_4 \,; \qquad 2FeCl_2 + Cl_2 = 2FeCl_3.$$

Chlorine reacts with ammonia, liberating nitrogen, but nitrogen trichloride is formed if chlorine is in excess.

$$3Cl_2 + 8NH_3 = 6NH_4Cl + N_2 \,; \qquad 3Cl_2 + NH_3 = NCl_3 + 3HCl.$$

In presence of water, chlorine can also oxidise by the addition of oxygen to a compound. Thus it converts sulphurous acid to sulphuric acid :

$$H_2SO_3 + H_2O + Cl_2 = H_2SO_4 + 2HCl.$$

Chlorine displaces sulphur from hydrogen sulphide and iodine from hydrogen iodide : $H_2S + Cl_2 = 2HCl + S$; $2HI + Cl_2 = 2HCl + I_2$ It can also displace bromine from a bromide and iodine from an iodide : $2KI + Cl_2 = 2KCl + I_2$; $2KBr + Cl_2 = 2KCl + Br_2$.

Expt.—Chlorine water is added to potassium iodide solution and then shaken with a little carbon disulphide—carbon disulphide dissolves the liberated iodine, forming a *violet layer*. The experiment is repeated with potassium bromide solution ; the liberated bromine colours the carbon disulphide layer *reddish brown*.

(vii) **Bleaching action of chlorine.**—*Chlorine bleaches vegetable colours in presence of moisture—dry chlorine does not bleach.* Moist chlorine liberates nascent oxygen : $H_2O + Cl_2 = 2HCl + O$.

The nascent oxygen oxidises the vegetable colouring matter and the colour is bleached, i.e., *chlorine bleaches by oxidation.*

Expt.—A green leaf, a piece of red cloth, a piece of printed paper brushed with writing ink,—all are placed, one in each, in a set of jars containing *moist* chlorine. All the articles are found to be bleached *except the prints.* The printer's ink contain free carbon which is not acted on by chlorine.

The experiment is repeated with dry chlorine but with a negative result.

(viii) Chlorine forms *additive compounds* with many unsaturated substances, e.g., $CO + Cl_2 = COCl_2$ (carbonyl chloride) : $SO_2 + Cl_2 =$

$C_2H_4 + Cl_2 = C_2H_4Cl_2$ (ethylene dichloride). sulphuril chloride SO_2Cl_2

Tests.—(*i*) Chlorine is detected by its greenish yellow colour, irritating smell and bleaching properties.

(*ii*) Chlorine liberates iodine from potassium iodide, which turns starch blue.

Uses.—(*i*) As a bleaching agent in paper and textile industries.

(*ii*) As a disinfectant in the sterilisation of water, and in dressing wounds—Carrel-Dakin solution used for the purpose is obtained by the action of chlorine upon washing soda.

(*iii*) As a poison gas, and for making poison gases, such as phosgene, mustard gas and chloropicrin:

(*iv*) For the manufacture of bleaching powder, hydrochloric acid, bromine, hypochlorite, and many chlorides such as $AlCl_3$, $MgCl_2$, $SnCl_4$, and PCl_5.

Manufacture of chlorine.—Chlorine is obtained as a by-product in the manufacture of caustic soda and sodium, by the electrolysis of brine and fused common salt respectively. It is stored and transported as a liquid under pressure in steel sylinders.

The manufacture of caustice soda by electrolysis is actually limited by the demand for chlorine, and hence chlorine is now never obtained commercially from hydrochloric acid by Weldon or Deacon processes, rather hydrochloric acid is now-a-days synthesised on a technical scale from chlorine and hydrogen. Hence the Weldon and Deacon processes are described in outline only.

Weldon Process.—Pyrolusite (mineral manganese dioxide containing about 10% ferric oxide) is heated with concentrated hydrochloric acid in a stone still by means of live steam—the evolved chlorine passes out through an exit pipe.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The commercial success of the process depends upon the regeneration of manganese dioxide. The spent liquor, containing manganous chloride, ferric chloride and undecomposed acid, is neutralised by limestone when the iron is also precipitated

$Ca(OH)_2$

as hydroxide, and then allowed to stand in a setting tank. The clear liquor from the top, containing manganous chloride, is syphoned off and then treated with 35—40% excess of milk of lime in an iron cylinder, air being simultaneously blown into the mixture which is heated to 60° by steam. Manganous hydroxide is oxidised by air to manganese dioxide which reacts with lime, giving the so-called Weldon mud, calcium manganite, CaO, MnO_2. Excess lime, prevents incomplete oxidation through the formation of manganous manganite, 2MnO, MnO_2. The Weldon mud is decomposed by HCl in the still over again and so the process continues.

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2$$

$$Mn(OH)_2 + Ca(OH)_2 + O = CaO, MnO_2 + 2H_2O ,$$

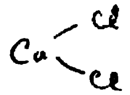
$$CaO, MnO_2 + 6HCl = CaCl_2 + MnCl_2 + 3H_2O + Cl_2$$

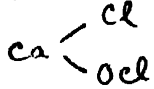
The conversion of hydrochloric acid to chlorine is 30% only.

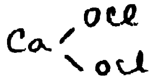
Deacon Process.—In this process hydrogen chloride is oxidised by air to chlorine and water in presence of cupric chloride catalyst at the optimum temperature of 450°C.

$$4HCl + O_2 \leftrightharpoons 2Cl_2 + 2H_2O$$

Dry HCl gas and air (1 : 4 by volumes) are preheated to about 200°C and then passed through a converter containing broken pieces of bricks soaked in cupric chloride solution—the catalyst is kept at 450°C. The gases after leaving the converter pass up a tower down which descends a stream of water which absorbs HCl vapours, and chlorine passes out. The conversion is about 60%. Hence it largely superseded the wasteful Weldon process. The chlorine obtained by the Deacon process is greatly diluted by nitrogen and contains about 10% chlorine only—the Weldon chlorine is however highly concentrated.







calsium hypochlorite

Bromine

Formula Br_2 ; b.p. 58.8 ; m.p. −7.3° ; atomic weight 79.916 ; atomic number 36 ; solubility 3.6 gm. in 100 gm. water at 20° ; density 3.19 at 0°.

Bromine was discovered by Balard in 1826 by chlorinating the mother liquors (called **bittern**) left after the crystallisation of salt from sea water—these liquors contained magnesium bromide : $MgBr_2 + Cl_2 = MgCl_2 + Br_2$.

General method of Preparation of Halogens.—Chlorine, bromine or iodine may be obtained by heating the corresponding halide with manganese dioxide and concentrated sulphuric acid. The reaction is :

$$MnO_2 + 2NaX + 3H_2SO_4 = MnSO_4 + 2NaHSO_4 + 2H_2O + X_2,$$

where X = Cl, Br or I. Fluorine cannot be prepared by this method.

Laboratory preparation of bromine.—A mixture of potassium bromide (5 gm.), manganese dioxide (15 gm.) and fairly strong sulphuric acid (100 c.c. of 50% strength) is carefully heated in a stoppered glass retort, the end of which communicates with a water-cooled receiver (p. 48). Bromine distils and condenses as a dark red liquid in the receiver.

$$MnO_2 + 2KBr + 3H_2SO_4 = MnSO_4 + 2KHSO_4 + 2H_2O + Br_2.$$

Bromine may also be obtained by passing chlorine into a strong solution of potassium bromide : $2KBr + Cl_2 = 2KCl + Br_2$.

Properties.—(i) Bromine is a highly poisonous, *dark* red heavy **liquid** with irritating smell and corrosive properties—*the only non-metal which is liquid at the ordinary temperature.*

The bromine vapour attacks the eyes and the liquid corrodes the skin.

(ii) It dissolves in water (only 3.6% at 20°), giving a reddish-coloured solution, called **bromine water** which, though fairly stable in the dark, liberates nascent oxygen in bright sunlight.

$$2Br_2 + 2H_2O = 4HBr + O_2.$$

Bomine water on cooling yields red crystalline *bromine hydrate*, $Br_2, 8H_2O$.

Bromine is readily soluble in such organic solvents as ether, alcohol, chloroform and carbon disulphide.

(iii) Bromine vapours (red in colour) do not burn but support the spontaneous combustion of many substances such as arsenic, antimony, phosphorus and potassium, yielding bromides.

Bomine directly unites with most metals and many non-metals yielding bromides, but *it is without action upon carbon, oxygen and nitrogen.*

Bromine is less active than chlorine but closely resembles it in chemical properties.

(iv) It reacts with hydrogen but less vigorously than chlorine. Bromine and hydrogen combine only when *heated*; a burning jet of hydrogen burns in bromine vapour, yielding hydrogen bromide.

$$H_2 + Br_2 = 2HBr.$$

(v) It resembles chlorine in its action upon caustic alkalis yielding bromide and **hypobromite** with a cold solution of an alkali, and bromide and **bromate** with the hot alkali.

$$Br_2 + 2NaOH \text{ (cold)} = NaBr + NaOBr + H_2O.$$
$$3Br_2 + 6NaOH \text{ (hot)} = 5NaBr + NaBrO_3 + 3H_2O.$$

Bromine dissolves in alkaline hydrogen peroxide solution, evolving oxygen:

$$H_2O_2 + 2NaOH + Br_2 = 2NaBr + 2H_2O + O_2.$$

(vi) Like chlorine, it is an oxidising agent. Thus it precipitates sulphur from hydrogen sulphide, liberates iodine from hydrogen iodide, and converts sulphurous acid to sulphuric acid. It can displace iodine from potassium iodide: $2KI + Br_2 = 2KBr + I_2$.

$$H_2S + Br_2 = 2HBr + S\ ; \qquad 2HI + Br_2 = 2HBr + I_2.$$
$$H_2SO_3 + Br_2 + H_2O = H_2SO_4 + 2HBr.$$

(vii) Bromine water has feeble bleaching properties; thus it bleaches litmus, and turns starch paper yellow.

(viii) Like chlorine, it gives addition products with unsaturated compounds: $C_2H_4 + Br_2 = C_2H_4Br_2$ (ethylene dibromide).

Tests.—Bromine is detected by its red colour and irritating smell: it dissolves in carbon disulphide, giving reddish-brown solution. Bromine turns starch yellow.

Uses.—(i) In the manufacture of coal tar dyes and bromides (used in medicine and in photography); in the extraction of gold.

(ii) In the preparation of ethylene dibromide (used in anti-knock petrol) and methyl bromide (for fire extinguishers) and in many organic syntheses.

(iii) In making *tear gases*; as a disinfectant and as an oxidising agent in the laboratory.

Bromine is kept in stoppered bottles. It severely corrodes the skin, which should be washed with petroleum if it comes in contact with bromine.

Manufacture of Bromine.—Bromine is obtained on a technical scale from the following sources.—(i) *Sea water.*—Waters of the Atlantic Ocean contains about 0.007% bromine, while the Dead Sea water contains about 0.042% of the element, mainly as bromides of alkali metals. (ii) *Spring water*—Spring water in Ohio contain about 3.4-3.9% magnesium bromide. (iii) *Carnallite* of Stassfurt deposits in Germany, $KCl,MgCl_2,6H_2O$, contains about 1 per cent of magnesium bromide.

Bromine from carnallite.—Carnallite is the most important source. The hot solution of carnallite deposits crystals of potassium chloride on cooling—the mother liquor, commonly called *bittern*, containing about 0.25% bromine as magnesium bromide is the commercial source for bromine. This is treated with chlorine, when bromine is liberated : $MgBr_2 + Cl_2 = MgCl_2 + Br_2$.

The hot mother liquor at 60° is allowed to descend down a tower packed with earthen ware balls (fig. 107) and connected with a chamber below. Streams of chlorine and steam are sent, via *the chamber*, up the tower. The bromine vapours leave the tower by an outlet at the top and condense in a spiral *earthen* cooling tube to a liquid which collects in a receiver. Any vapours of bromine which escape condensation is absorbed in a tower in moist iron filings which forms iron bromide.

The spent liquor flowing into the chamber contains some dissolved bromine ; this is recovered by passing a current of steam which carries the bromine vapours away through the tower.

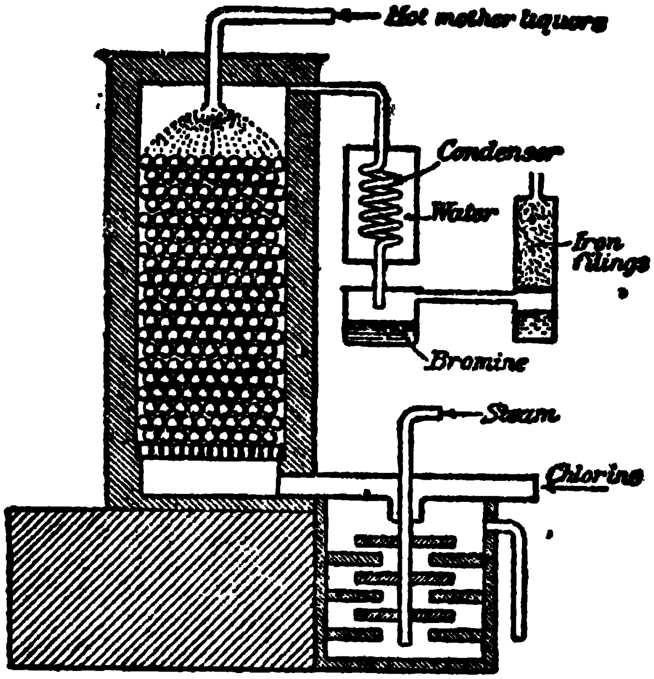


Fig. 107

The residual liquid from the waters of the Dead Sea after the crystallisation of potassium and magnesium chloride and the *bittern* from some American salt mines in Ohio and Michigan after crystallisation of common salt are similarly treated for bromine.

Bromine from Sea Water.—To meet the increasing demand of bromine, it is nowadays extracted from sea water on the Atlantic coast of America. The bromine is liberated by the action of chlorine ; but owing to its great dilution, it is appreciably hydrolysed, yielding bromide and hypobromite :

$$Br_2 + H_2O \rightleftharpoons HBr + HOBr.$$

The hydrolysis is prevented by previous acidification with sulphuric acid—about 0.25 lb. of concentrated acid being added to each ton of sea-water. The sea-water is acidified and chlorinated. The liberated bromine is removed from the water by a current of air, and is absorbed in active charcoal, from which it is recovered by a current of steam.

The bromine that is blown by a current of air, may also be absorbed in hot caustic soda solution, forming bromide and bromate. This is acidified when bromine is set free :

$$3Br_2 + 6NaOH = NaBrO_3 + 5NaBr + 3H_2O.$$
$$NaBrO_3 + 5NaBr + 3H_2SO_4 = 3Na_2SO_4 + 3Br_2 + 3H_2O.$$

1800 gallons of sea-water are treated to obtain 1 lb. of bromine.

Purification.—Commercial bromine usually contains water, chlorine and iodine as impurities. It is distilled over a mixture of potassium bromide and zinc oxide—the potassium bromide removes chlorine, and zinc oxide iodine. The water is removed by distillation over concentrated sulphuric acid. It may be dried with quick lime or anhydrous calcium bromide.

Iodine

Fomula I_2. Atomic weight 126.92. Atomic number 53. Solubility in water at 0° 0.016% only. Density, 9.94. Melting point 113.9°. Boiling point 184.4°.

Laboratory preparation.—In the laboratory iodine is prepared by heating a mixture of potassium iodide, manganese dioxide, and 50 per cent sulphuric acid in a stoppered glass retort (p. 48) which communicates with a water-cooled receiver. Iodine is liberated on heating the retort ; it sublimes as violet vapours and condenses in the receiver as black shining crystals :

$$MnO_2 + 2KI + 3H_2SO_4 = MnSO_4 + 2KHSO_4 + I_2 + 2H_2O.$$

Iodine may also be obtained by passing chlorine into a strong solution of potassium iodide : $2KI + Cl_2 = 2KCl + I_2$.

Sublimation of Iodine.—An intimately ground mixture of iodine (about 10 gms.) and potassium iodide (about 5 gms.) is carefully heated in a basin on a sand bath—a larger shallow dish filled with cold water, is placed on the top of the basin. On cautious heating the bottom of the water-cooled dish becomes covered with shining crystals of iodine. The basin may also be cover with a funnel (p. 51) when iodne deposits on the inside wall.

Properties.—(i) Dark grey shining crystals ; the molecular formula of the vapour up to 700°C is I_2 but thermal dissociation occurs above 700°C : $I_2 \rightleftharpoons 2I$.

On dropping a few crystals of iodine in a heated flask, the latter is filled with violet vapours of iodine.

(ii) Very slightly soluble in water (1 part in 500 parts), iodine readily dissolves in aqueous potassium iodide giving a brown solution, due to the formation of potassium tri-iodide : $KI + I_2 \rightleftharpoons KI_3$.

It is also freely soluble in organic solvents such as alcohol, chloroform, benzene, ether and carbon disulphide.

In water, ether and alcohol, iodine forms brown solutions, in benzene and chloroform purple solutions, and in carbon disulphide a violet solution.

Iodine resembles other halogens in chemical properties, but is much less active.

(iii) Iodine vapours do not burn, but very much like chlorine, they support the combustion of white phosphorus, arsenic, antimony, etc., though less energetically :

$$2P + 3I_2 = 2PI_3.$$

Iodine directly combines with most metals, but of the non-metals, it directly unites only with *hydrogen, phosphorus and the halogens*, yielding the *inter-halogen compounds* with the latter, namely, IF_5, IF_7, ICl_3, and IBr.

On rubbing mercury and iodide together in a mortar, a green mercurous iodide, Hg_2I_2 is formed if the mercury is in excess, and a red mercuric iodide, HgI_2, if the iodine is in excess : $Hg + I_2 = HgI_2$.

(iv) It has affinity for hydrogen ; but the affinity is much less compared to other halogens ; thus a mixture of hydrogen and iodine combines when heated in presence of a platinum catalyst, forming hydrogen iodide—*the reaction is reversible* : $H_2+I_2 \rightleftharpoons 2HI$.

(v) **Action on alkalis.**—It resembles chlorine in its reaction with alkalis—cold alkali giving iodide and **hypoiodite** ; hot alkali producing iodide and **iodate.** The hypoiodite rapidly passes into iodate and iodide on keeping.

$$I_2+2KOH = KI+KOI+H_2O \; ; \; 3I_2+6KOH = 5KI+KIO_3+3H_2O$$

Iodine dissolves in alkaline solution of hydrogen peroxide, giving off oxygen.

$$H_2O_2 + 2NaOH + I_2 = 2NaI + 2H_2O + O_2.$$

(vi) Iodine is a mild oxidising agent. Sulphur separates when hydrogen sulphide is passed into a suspension of iodine in water. It oxidises sulphurous acid to sulphuric acid, stannous chloride to stannic chloride, and arsenious acid to arsenic acid :

$$I_2 + H_2S = 2HI + S \; ; \quad H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI.$$

$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2HI.$$

(vii) Since iodine is practically insoluble in water, it has no bleaching properties.

(viii) **It gives a deep-blue colour with starch solution**—the colour disappears on heating and reappears on cooling.

(ix) It has no action upon potassium chloride or bromide, but chlorine or bromine can liberate iodine from potassium iodide, hence it is less active than these elements.

$$2KI + Cl_2 = 2KCl + I_2 \; ; \quad 2KI + Br_2 = 2KBr + I_2.$$

Iodine can however liberate chlorine from potassium chlorate and chloric acid : $2KClO_3 + I_2 = 2KIO_3 + Cl_2$.

(x) Iodine reacts with sodium thiosulphate, $Na_2S_2O_3$, solution, yielding sodium tetrathionate and sodium iodide—a reaction used in estimating iodine (*iodometry*, as it is called).

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 \text{ (sodium tetra thionate) } + 2NaI.$$

(xi) Unlike other halogens, iodine may be oxidised by concentrated nitric acid to iodic acid. $3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O$.

Tests.—(i) Iodine yields violet vapours on heating. Iodine gives a blue colour with starch solution—1 part of iodine in 5,000,000 of water may be detected.

(ii) It dissolves in carbon disulphide, forming a violet solution.

(iii) It produces yellow crystals of iodoform of characteristic smell, when warmed with ethyl alcohol and caustic soda.

Manufacture of Iodine.—Sources.—(i) **Deep sea weeds** (*laminaria*)—Iodine does not occur free in nature ; sea-water contains traces of iodine—about 0.001 per cent—mainly as iodide ; this is absorbed by certain sea weeds. The sea-weeds are drift ashore during storms. The ash of burnt sea-weed, called **kelp,** contains about 1 per cent combined iodine.

(ii) **Caliche.**—Crude Chile salt petre, called CALICHE, contains about 0.2 per cent sodium iodate and forms and important source of iodine.

(iii) **Petroleum brines.**—Californian brines, containing about 30—70 parts of iodine as iodide per million parts of it, is now one of the principal sources of iodine and has reduced the price of iodine by more than half.

(i) **From kelp.**—The ash from burnt sea-weeds, *kelp*, as it is called, is lixiviated with hot water and the solution is concentrated, when the less soluble sodium and potassium sulphates, common salt potassium chloride crystallise out—the more soluble sodium and potassium iodides remain in the mother liquor. The mother liquor is mixed with manganese dioxide and fairly strong sulphuric acid and heated in cast iron pots. The liberated iodine sublimes and condenses in a series of earthenware receivers, called *aludels*. The iodine is purified by sublimation. 1 ton of kelp yields about 12 lb. of iodine.

$$MnO_2 + 2NaI + 3H_2SO_4 = 2NaHSO_4 + MnSO_4 + 2H_2O + I_2$$

The element was discovered by this method by Courtois in 1811. The process works in France, Japan and Great Britain.

(ii) **From caliche.**—The mother liquor of *caliche*, left after the crystallisation of sodium nitrate, contains about 3 gms. of sodium iodate per litre. This is treated with the calculated amount of sodium bisulphite solution when iodine deposits. The iodine is separated, pressed, dired and purified by sublimation. Sodium bisulphite reduces a portion of iodate to iodide ; the acidity of sodium bisulphate formed liberates hydriodic and iodic acids which react depositing iodine :

$$5NaIO_3 + 15NaHSO_3 = 5NaI + 15NaHSO_4.$$
$$NaIO_3 + 5NaI + 6NaHSO_4 = HIO_3 + 5HI + 6Na_2SO_4.$$
$$HIO_3 + 5HI = 3I_2 + 3H_2O.$$

$$6NaIO_3 + 15NaHSO_3 = 3I_2 + 3H_2O + 9NaHSO_4 + 6Na_2SO_4.$$

(iii) **From Petroleum Brines.**—Iodine is recovered from oil field brines by the activated carbon process. The brine is treated with sodium nitrite and sulphuric acid, which liberates iodine.

$$2NaNO_2 + 2NaI + 4H_2SO_4 = 4NaHSO_4 + 2NO + I_2 + 2H_2O.$$

The iodine concentration being very low, the solution is agitated with activated charcoal which adsorbs free iodine. The carbon is filtered off and then leached with hot alkali, when the iodine is converted into iodate and iodide.

$$3I_2 + 6NaOH = 5NaI + NaIO_3 + 3H_2O.$$

This solution is then concentrated by evaporation, and acidified when iodine is set free—the latter sublimes and condenses in earthenware receivers. The process does not work since 1934.

In a recent method the oil field brine (containing 60-65 parts of iodine per million parts of water) is acidified with sulphuric acid and then injected with chlorine gas—the liberated iodine is blown out by an air current. From the iodine-laden air the iodine is absorbed in a solution of hydriodic and sulphuric acids which is continuously fed with sulphur dioxide. The iodine is reduced to HI by the SO_2 :

$$I_2\ (air) + SO_2 + 2H_2O = 2HI + H_2SO_4.$$

The hydriodic acid—sulphuric acid liquor is then treated with chlorine when iodine is precipitated, and filtered : $2HI + Cl_2 = 2HCl + I_2$.

The iodine is melted in strong sulphuric acid (over 60%) to char organic matter and remove water, and then purified by sublimation.

By another method iodine is precipitated from the oil well brines as silver iodide and then converted into ferrous iodide from which chlorine liberates iodine. The silver is recovered, converted to silver nitrate and used over again :

$$NaI + AgNO_3 = AgI + NaNO_3.$$
$$2AgI + Fe = FeI_2 + 2Ag\ ;\ FeI_2 + Cl_2 = FeCl_2 + I_2.$$

Purification.—Crude iodine contains moisture and generally the impurities iodine chloride, ICl, iodine bromide, IBr and iodine cyanide, ICN, which cannot be removed by sublimation, because of their volatility. These impurities are removed by heating a well ground mixture of crude iodine, lime (which retains moisture) and potassium iodide (which removes chlorine, bromine and cyanogen)—pure iodine sublimes : $ICl + KI = KCl + I_2$.

Further purification is effected by dissolving the sublimed iodine in potasium iodide solution and then precipitating it by dilution with water—the precipitated iodine is finally dried in vacuo over conc. H_2SO_4.

Uses.—(i) In the manufacture of certain drugs, and dyes. Iodoform, CHI_3, is used as an anti-septic for dressing wounds.

(ii) As a disinfectant as **tincture of iodine** (solution of iodine in potassium iodide and rectified spirit—1 oz. each of KI, I_2 and water in one pint of rectified spirit).

(iii) In iodometry and organic syntheses. The practical use of iodometry is in the estimation of oxidising agents such as hydrogen peroxide which liberates iodine from an acidified solution of potassium iodide—the iodine being titrated with sodium thiosulphate, using starch as an indicator.

Iodine compounds also play an important part in the body—THYROXIN is an iodine compound secreted by the thyroid gland ; goitre, a disease of the gland, is due to iodine deficiency. Use of table salt containing 0.023% KI is advocated to reduce the prevalence of goitre.

HYDRACIDS OF HALOGENS

Hydrochloric acid (Muriatic acid)

Formula HCl ; mol. wt. 36.465 ; b. p.—85°C ; m. p.—111.4 ; solubility per c.c. of water : 525 c.c. at 0°C and 458 c.c. at 15°C.

History and occurrence.—The knowledge of the solution of hydrogen chloride is attributed to the alchemist Geber of the 8th century. The gas hydrogen chloride was discovered by Priestley in 1727 but its true nature was established by Davy in 1810. The gas is occasionally found in volcanic gases ; the gastric juice contains aqueous solution of the acid (0.2—0.4 per cent).

Laboratory preparation.—Hydrochloric acid is prepared by gently heating common salt with concentrated sulphuric acid—the reaction is :

(i) $NaCl + H_2SO_4 = NaHSO_4 + HCl$ (150°—200°C.)

(ii) $NaCl + NaHSO_4 = Na_2SO_4 + HCl$ (over 500°C.)

The reaction (i) occurs on gentle warming, but the reaction (ii) does not take place until the temperature is raised to above 500°C.

Common salt is taken in a flask fitted with a thistle funnel and a delivery tube. Fairly concentrated sulphuric acid is poured down the funnel when a quick evolution of hydrogen chloride gas occurs. When this slackens, the flask is gently heated. The gas is dried by bubbling through concentrated sulphuric acid and collected by the upward displacement of air or over mercury.

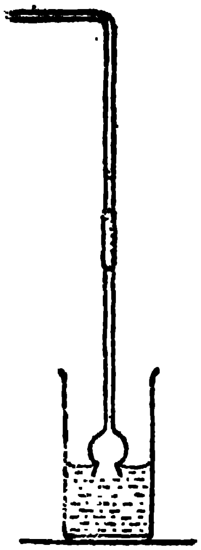


Fig. 108

If a solution of hydrogen chloride is required, the end of the delivery tube is connected with the stem of a funnel which dips just below the surface of water in a beaker—the gas dissolves in water, yielding an aqueous solution, (fig. 108).

Pure hydrogen chloride is obtained by the action of water upon silicon tetrachloride : $SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl$.

A convenient supply of gas is readily obtained by dropping concentrated hydrochloric acid upon concentrated sulphuric acid taken in a flask.

Properties.—(i) A colourless gas with a choking smell and strongly fuming in moist air, hydrogen chloride is 1.27 times heavier than air ; it neither burns nor supports burning.

(ii) It is highly soluble in water. The solubility of the gas may be shown by *fountain experiment.*

A solution of the gas in water is known as hydrochloric acid. The saturated solution has a density of 1.231 at 15°C and contains 43 per cent hydrogen chloride.

Any solution of hydrochloric acid, on distillation, yields an ultimate residue of 20.24% hydrogen chloride, boiling at 110°C ; this is a *constant boiling mixture.*

(iii) In aqueous solution hydrogen chloride acts like a strong monobasic acid ; the solution readily dissolves base metals, liberating hydrogen and forming chlorides *containing the metal in the lowest (ous) state of valency :*

$$Sn + 2HCl = SnCl_2 + H_2 ; \quad Fe + 2HCl = FeCl_2 + H_2.$$

The metals also react with hydrochloric acid gas, yielding anhydrous chloride—burning sodium continue burning in gaseous hydrochloric acid. Noble metals such as gold, platinum, etc., are not attacked by the acid. Copper slowly dissolves in hot and concentrated acid, and silver is slowly attacked *in presence of air only.*

$$2Cu+8HCl = H_2+2H_3CuCl_4 ; \quad 4Ag+4HCl+O_2 = 4AgCl+2H_2O.$$

Liquid hydrogen chloride does not conduct electricity and is without action upon metals in absence of water—aluminium, however, dissolves in it.

(iv) It reacts with metallic oxides and hydroxides, yielding salt and water : it combines with ammonia, in presence of trace of moisture, forming dense white fumes of ammonium chloride ; it decomposes carbonates, liberating carbon dioxide :

$$CuO+2HCl = CuCl_2+H_2O ; \quad NaOH+HCl = NaCl+H_2O.$$

$$NH_3+HCl = NH_4Cl ; \quad CaCO_3+2HCl = CaCl_2+H_2O+CO_2.$$

(v) It is readily oxidised to chlorine by manganese dioxide or potassium permanganate. $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$.

Tests.—(i) Heated with manganese dioxide and concentrated sulphuric acid, hydrogen chloride or any metallic chloride, yields the greenish yellow gas chlorine.

(ii) In aqueous solution hydrogen chloride or any soluble metallic chloride gives a curdy white precipitate of silver chloride with silver nitrate solution—the precipitate is soluble in ammonia but insoluble in nitric acid.

$$HCl + AgNO_3 = HNO_3 + AgCl ; \quad AgCl + 2NH_3 = [Ag(NH_3)_2]Cl.$$

Uses.—Hydrochloric acid stands second only to sulphuric acid in its uses in industry. It is used : (i) in making metallic chlorides, (ii) in dyeing and calico-printing and in medicine, (iii) in pickling baths to remove oxide scale from sheet iron which is to be tinned, galvanised or made into enamel ware, (iv) in making glue from cartilage, and glucose from starch. Hydrochloric acid is a reagent in the laboratory. It is used in aqua regia to dissolve gold and platinum. C.P. (chemically pure) concentrated acid contains 37.58 to 38.95 per cent HCl and has a density of 1.190 to 1.196.

Manufacture of Hydrochloric Acid.—(ii) **From common salt.**—Hydrochloric acid was formerly obtained by the action of sulphuric acid upon common salt, as a by-product in the manufacture of sodium carbonate by the *Le blanc process* which is now obsolete ; but it is still obtained by this method, owing to the demand for sodium sulphate.

On a technical scale hydrochloric acid is manufactured by heating common salt and concentrated sulphuric acid in a cast iron pot A ; the evolved hydrogen chloride is absorbed in water in a set of absorbers (I, II and III) made of clay with acid proof glaze (fig. 109).

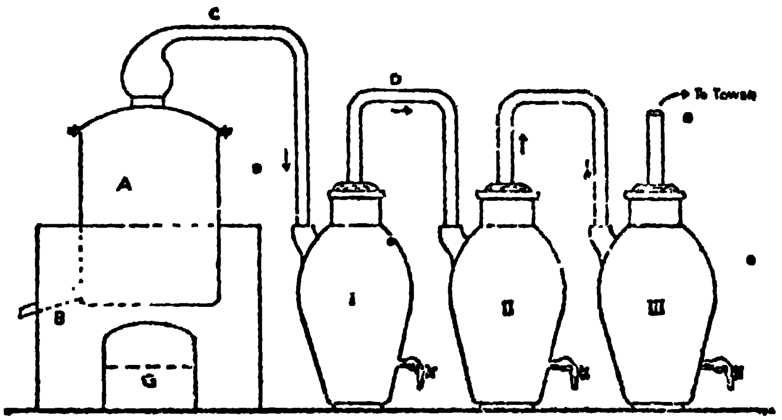


Fig. 109

The commercial acid has a density of 1.14 and contains about 28% acid. The usual impurities in the commercial acid are arsenious oxide, ferric chloride and sulphuric acid—arsenic can be avoided by using sulphuric acid free from arsenic. The acid is purified by distilling over a mixture of barium chloride (to convert sulphuric acid into barium sulphate) and copper fillings (to reduce ferric chloride to non-volatile ferrous chloride).

(i) **Synthetic method.**—Hydrochloric acid is nowadays manufactured by the combustion of hydrogen and chlorine which are obtained as by-products in the manufacture of caustic soda by the electrolytic process. A mixture of nearly equal volumes of hydrogen and chlorine —a slight excess of hydrogen being used for the complete conversion of chlorine into hydrogen chloride, is fed into a burner, similar to oxyhydrogen blowpipe, set in a silicabrick combustion chamber, (fig. 110). The resulting hydrogen chloride is cooled and then absorbed in water in in an absorption tower until the solution is saturated—the acid obtained is very pure. Chlorine may also be made to combine with hydrogen in presence of activated charcoal to form hydrogen chloride :

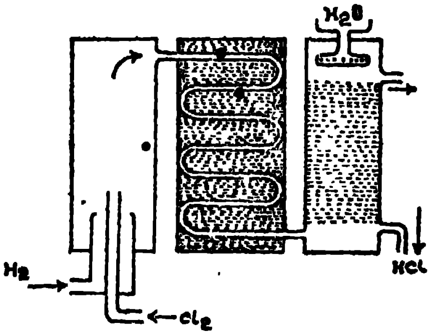


Fig. 110

$$H_2 + Cl_2 = 2HCl.$$

Composition of hydrogen chloride.—The composition of hydrogen chloride may be determined either by *analysis* or by *synthesis.*

(i) **By analysis.**—(a) When a concentrated aqueous solution of hydrochloric acid is electrolysed, chlorine is liberated at the anode and hydrogen at the cathode.

A dilute solution of the acid, it must be remembered, yields hydrogen and oxygen, on electrolysis.

The electrolysis is carried out in a three-limbed voltameter—the central tube carrying a funnel acts as the reservoir of the acid and the two graduated side-tubes, fitted with *gascarbon electrodes* (chlorine attacks platinum) at the bottom, are the collecting vessels (fig. 111). The apparatus is filled with the acid through the funnel and the electrolysis carried out by connecting the carbon electrodes with the poles of a battery. Hydrogen collects at the cathode but the chlorine liberating at the anode, dissolves in water, *until the solution is saturated with chlorine*—very little chlorine collects at the anode before saturation. The hydrogen, collected at the cathode, is allowed to pass out and the apparatus is then filled with the solution thus saturated with chlorine and the process of electrolysis continued. It is found that hydrogen and chlorine collect in equal volumes in the two limbs. Hence *hydrochloric acid contains equal volumes of hydrogen and chlorine.*

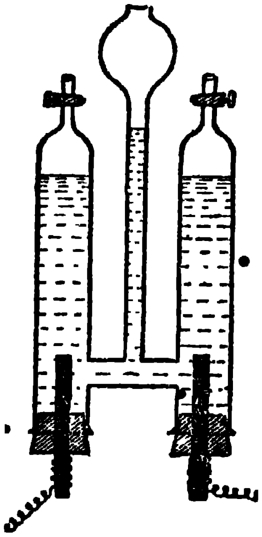


Fig. 111

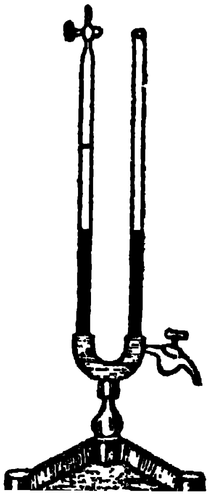


Fig 112

(b) Hydrogen chloride may be shown to contain half its volume of hydrogen by its reaction with sodium amalgam. A measured volume of hydrogen chloride is collected in a graduated tube over mercury (fig. 112) and a pellet of sodium amalgam introduced into it. The reaction over, mercury stands at half its original volume—the residual gas in the tube is found to be hydrogen. Hence hydrogen chloride contains half its volume of hydrogen.

$$\text{Sodium-amalgam} + 2HCl = \text{sodium chloride} + H_2.$$

But the hydrogen chloride gas contains equal volumes of hydrogen and chlorine. Hence 2 volumes of hydrogen chloride = 1 volume of hydrogen + 1 volume of chlorine.

(ii) **By Synthesis.**—A glass tube (fig. 113) provided with stop-cocks at the two ends is made into two equal halves by a three way stop-cock. The two halves are filled with hydrogen and chlorine, one gas in each half. The gases are mixed by opening the central tap and the mixture exposed to diffused sun-light for about two days. On opening one of the end stop-cocks under mercury, *no change of volume takes place* ; but when opened under water, it rushes up and completely fills the tube, showing that there is no uncombined hydrogen. The aqueous solution does not liberate iodine from potassium iodide and hence contains no free chlorine ;

the solution is found to be acidic and yields a white precipitate with silver nitrate and hence it is hydrochloric acid. This shows that the whole of hydrogen and chlorine have combined and the gas obtained after the reaction consists of hydrogen chloride only. Hence :

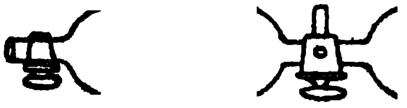


Fig. 113

2 vols. hydrogen chloride = 1 vol. hydrogen + 1 vol. chlorine.

Or, 2 mols. hydrogen chloride = 1 mol. hydrogen + 1 mol. chlorine. (By Avogadro's hypothesis).

Or, 1 mol. hydrogen chloride = ½ mol. or 1 atom of H_2 + ½ mol. or 1 atom of Cl_2.

Hence, the formula of hydrogen chloride is HCl. This agrees with the molecular weight 36.5, arrived at experimentally from its vapour density.

Hydrobromic and hydriodic acids

Hydrofluoric and hydrochloric acids can be prepared by the action of concentrated sulphuric acid upon a corresponding halide. But hydrobromic and hydriodic acids cannot be similarly prepared by heating a bromide or an iodide with concentrated sulphuric acid, since these acids (unlike HF and HCl) are oxidised by sulphuric acid, so that bromine or iodine and sulphur dioxide are only obtained.

$$2KBr + 2H_2SO_4 = 2KHSO_4 + 2HBr$$

$$2HBr + H_2SO_4 = Br_2 + 2H_2O + SO_2$$

$$2KBr + 3H_2SO_4 = 2KHSO_4 + Br_2 + 2H_2O + SO_2$$

$$2KI + 3H_2SO_4 = 2KHSO_4 + I_2 + 2H_2O + SO_2.$$

Hydrobromic Acid.—Hydrogen and bromine vapour do not readily react even in bright sun-light, but combination begins at 200°C in presence of platinum as a catalyst to yield hydrogen bromide :

$$H_2 + Br_2 \rightleftharpoons 2HBr.$$

Dry hydrogen is bubbled through bromine in a wash-bottle heated to 40 to 50°C by a bath of hot water, and the mixture of hydrogen and bromine vapour is passed through a hard glass tube containing platinised asbestos heated to 200°C, where the synthesis of hydrogen bromide occurs. The hydrogen bromide passes through a tower packed with moist red phosphorus to remove any free bromine vapour, and then dried by fused calcium bromide, and cooled in liquid air when hydrogen bromide solidifies and excess of hydrogen passes on.

Laboratory preparation—Hydrogen bromide is prepared in the laboratory by the action of bromine upon a mixture of red phosphorus and water. Phosphorus tri- and penta-bromides first formed are decomposed (hydrolysed) by water, yielding hydrogen bromide and phosphorus and phosphoric acids :

$$2P + 3Br_2 = 2PBr_3 ; \quad 2P + 5Br_2 = 2PBr_5.$$

$$PBr_3 + 3H_2O = H_3PO_3 \text{ (phosphorous acid)} + 3HBr.$$

$$PBr_5 + 4H_2O = H_3PO_4 \text{ (phosphoric acid)} + 5HBr.$$

Red phosphorus and water are taken in a flask (fig. 114) fitted with a tap-funnel and a delivery tube. On *cautiously* adding bromine from the funnel, vigorous reaction takes place with evolution of hydrogen bromide. Towards the end of the reaction the flask is gently heated. The gas is freed from (i) accompanying bromine vapours by passing through a U-tube *containing the moist glass pieces and red phosphorus*, and (ii) moisture by passing through a second U-tube containing calcium chloride, and then collected by the upward displacement of air. The gas may be dried by calcium chloride or bromide and collected over mercury.

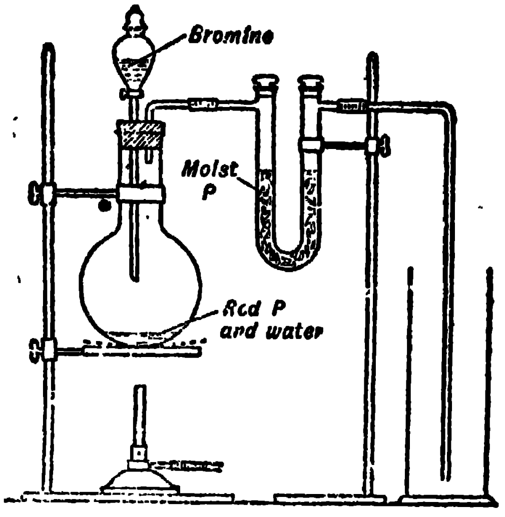


Fig. 114

An aqueous solution of hydrobromic acid may be obtained by connecting the delivery tube with the stem of a funnel which dips just below the surface of water in a beaker —hydrobromic acid is absorbed by water, giving an aqueous solution.

An aqueous solution may also be obtained by passing sulphuretted hydrogen or sulphur dioxide through bromine water. Sulphur is filtered off.

$$H_2S + Br_2 = 2HBr + S \; ; \quad SO_2 + 2H_2O + Br_2 = 2HBr + H_2SO_4.$$

Properties.—HBr resembles HCl in most of its properties.

(i) A colourless heavier-than-air gas with irritating smell, hydrogen bromide is very soluble in water—solubility, 600 volumes at 0°, giving a solution of 68% HBr. It forms a constant boiling mixture of 47.6 per cent hydrogen bromide, boiling at 126°.

(ii) The aqueous solution is strongly acid and dissolves metals and bases in the same way as hydrochloric acid.

(iii) Less stable than hydrochloric acid, it is more readily-oxidised —the aqueous solution is decomposed by air in presence of sunlight :

$$4HBr + O_2 = 2H_2O + 2Br_2.$$

Like HCl, it is easily decomposed by oxidising agents, such as manganese dioxide and potassium permanganate, but unlike HCl, it is also attacked by other oxidising agents, such as chlorine and concentrated sulphuric acid.

$$2HBr + Cl_2 = 2HCl + Br_2 \; ; \quad H_2SO_4 + 2HBr = Br_2 + 2H_2O + SO_2.$$

Tests.—(i) Hydrogen bromide or any metallic bromide, when heated with concentrated sulphuric acid yields red vapours of bromine.

(ii) Chlorine water liberates bromine from an aqueous solution of hydrogen bromide or any metallic bromide—the liberated bromine dissolves in carbon disulphide, imparting a reddish brown colour to the solution.

(iii) An aqueous solution of hydrogen bromide or any soluble metallic bromide gives a pale yellow precipitate of silver bromide with silver nitrate—the precipitate is insoluble in nitric acid but difficultly soluble in ammonia.

$$HBr + AgNO_3 = AgBr + HNO_3$$

Potassium Bromide.—(a) Hot caustic potash solution reacts with bromine, yielding a mixture of bromide and bromate. The solution is evaporated, and the residue ignited with powdered charcoal when the bromate is reduced to bromide. The mass is extracted with water—the solution on concentration deposits colourless crystals of potassium bromide. $2KBrO_3 + 3C = 2KBr + 3CO_2$.

(b) Iron bromide, formed by the action of bromine vapour upon moist iron filings (during the manufacture of bromine) is decomposed by potassium carbonate, when iron precipitates as hydroxide and is filtered off—the filtrate is crystallised for potassium bromide.

$$Fe_3Br_8 + 4K_2CO_3 + 4H_2O = Fe_3(OH)_8 + 8KBr + 4CO_2.$$

Potassium bromide is used in medicine (to induce sleep and to remove nervousness), and in photography. Ammonium bromide is formed by the action of bromine on cooled solution of ammonia : $8NH_3 + 3Br_2 = 6NH_4Br + N_2$.

Hydriodic acid

Preparation.—(i) Hydrogen iodide may be synthesised by passing a mixture of hydrogen and iodine vapour over a heated platinum catalyst—the hydrogen iodide is easily dissociated by heat. $H_2 + I_2 \leftrightharpoons 2HI$.

(ii) In the laboratory hydrogen iodide is prepared by a method similar to that for hydrogen bromide. Water is to be cautiously added from the tap-funnel into a mixture of red phosphorus and iodine taken in the flask—*iodine being a solid cannot be added like bromine from the funnel.* Phosphorus tri-iodide first formed is hydrolysed by water-yielding hydrogen iodide and phosphorous acid.

The hydrogen iodide is collected by the upward displacement of air. The gas attacks mercury and hence cannot be collected over the same : $PI_3 + 3H_2O = 3HI + H_3PO_3$.

(iii) Hydrogen iodide may also be prepared by heating potassium iodide with phosphoric acid. $3KI + H_3PO_4 = K_3PO_4 + 3HI$. Sulphuric acid cannot be used, since it oxidises hydrogen iodide to iodine.

$$2HI + H_2SO_4 = 2H_2O + I_2 + SO_2.$$

(iv) An aqueous solution of hydrodic acid is obtained by the the absorption of the gas in water in the usual way,as in the case of hydrobromic acid.

It may also be obtained by passing hydrogen sulphide into a suspension of iodine in water—the precipitated sulphur is filtered off : $H_2S + I_2 = 2HI + S$.

Properties.—HI resembles HBr in most of its properties.

(i) A colourless, heavier-than air gas with irritating odour and fuming strongly in air, hydrogen iodide is highly soluble in water, giving a solution containing 90 per cent of HI at 0°. Its constant boiling mixture contains 57 per cent HI, boiling at 126°. The aqueous solution is strongly acid.

(ii) It is readily decomposed into its elements on heating or on exposure to sun light ; violet vapours of iodine are evolved on introducing a heated glass rod into a jar of hydriodic acid.

$$2HI \rightleftharpoons H_2 + I_2.$$

(iii) *It is a strong reducing agent ;* it is readily attacked by oxidising agents, such as air, nitric acid, hydrogen peroxide, chlorine, sulphuric acid, etc. which also attack hydrobromic acid ; thus a colourless solution of hydriodic acid turns brown on exposure to air :

$$4HI+O_2 = 2H_2O+2I_2 ; \quad 2HI+H_2O_2 = 2H_2O+I_2.$$
$$2HNO_3+2HI = 2H_2O+I_2+2NO_2 ; \quad 2HI+Cl_2 = 2HCl+I_2.$$

Since hydrogen iodide is less stable than hydrogen bromide, the former is attacked by oxidisng agents such as ferric salts, cupric salts, nitrous acid, etc. which do not affect the latter :

$$2FeCl_3 + 2HI \rightleftharpoons 2FeCl_2 + 2HCl + I_2 ;$$
$$2CuSO_4 + 4HI = 2H_2SO_4 + Cu_2I_2 + I_2.$$
$$2HNO_2 + 2HI = 2H_2O + 2NO + I_2.$$

Hydriodic acid is a useful reducing agent, particularly in organic chemistry.

Tests.—(*i*) Hydroiodic acid or any metallic iodide, on being heated with concentrated sulphuric acid yields violet vapours of iodine.

(*ii*) Chlorine water liberates iodine from an aqueous solution of hydriodic acid or any metallic iodide, which dissolves in carbon disulphide, imparting a violet colour to the solution. $2HI + Cl_2 = 2HCl + I_2$.

(*iii*) An aqueous solution of hydriodic acid or any metallic iodide gives a yellow precipitate of silver iodide with silver nitrate—the precipitate is insoluble both in nitric acid and ammonia. $HI + AgNO_3 = AgI + HNO_3$.

Potassium Iodide.—(*i*) Hot concentrated caustic potash reacts with iodine, yielding a mixture of iodide and iodate. The solution is evaporated to a solid residue which is then reduced with charcoal, as in the preparation of potassium bromide. The mass is extracted with water and the solution crystallised for potassium iodide.

$$2KIO_3 + 3C = 2KI + 3CO_2.$$

(*ii*) Ferrous iodide, produced by interaction between iodine and moist iron filings, is decomposed by potassium carbonate, yielding potassium iodide and insoluble ferrous carbonate which is filtered off ; the filtrate is crystallised for potassium iodide·

$$FeI_2 + K_2CO_3 = FeCO_3 + 2KI.$$

It is used in medicine and photography. It reacts with cupric salt, precipitating cuprous iodide and liberating iodine—a reaction used for the volumetric estimation of copper. $2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2$.

Composition of Hydrogen Bromide or Iodide.—Hydrogen bromide or iodide can be shown to contain half its volume of hydrogen by adding sodium amalgam to a known volume of the gas in a graduated tube over mercury, as in the case of hydrochloric acid. 1 volume of hydrogen bromide contains ½ volume hydrogen ; hence 1 molecule hydrogen bromide contains ½ molecule or 1 atom hydrogen.

Hence, the formula HBr*x*, but the molecular wt. is 81, its vapour density being 40.5. $\therefore$ $1 + 80x = 81$ whence $x = 1$.

Hence the formula for hydrogen bromide is HBr. The formula for hydrogen iodide may be deduced similarly.

Oxides and Oxyacids of Chlorine

Chlorine does not combine directly with oxygen, but several oxides have been obtained by indirect means.

Oxides	Oxyacids
Chlorine monoxide, Cl_2O, gas	Hypochlorous acid, HOCl
Chlorine dioxide, ClO_2, gas	Chlorous acid, $HClO_2$
Chlorine hexoxide, Cl_2O_6, liquid	Chloric acid, $HClO_3$
Chlorine heptoxide, Cl_2O_7, liquid	Perchloric acid, $HClO_4$.

HOCl, $HClO_2$ and $HClO_3$ are known only in solution ; $HClO_4$ is a liquid.

Chlorine Monoxide and Hypochlorous acid.—When dry chlorine is passed over cooled precipitated mercuric oxide, the anhydride of hypochlorous acid, Cl_2O is obtained as a brownish yellow gas, which condenses ni a freezing mixture to an organge coloured liquid. With water, it yields hypochlorous acid ; unstable the gas explodes on heating. $2Cl_2 + 2HgO = HgO,HgCl_2 + Cl_2O$.

$$2Cl_2O = 2Cl_2 + O_2 \qquad Cl_2O + H_2O = 2HOCl.$$

An aqueous solution of hypochlorous acid is prepared by shaking chlorine water with precipitated yellow mercuric oxide and filtering from the basic mercuric chloride.

$$2Cl_2 + 2HgO + H_2O = HgO,HgCl_2 + 2HOCl.$$

It may also be prepared by passing chlorine into a suspension of chalk or sodium bicarbonate until the latter goes into solution.

$$2Cl_2 + 2H_2O = 2HCl + 2HOCl.$$

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

$$2Cl_2 + CaCO_3 + H_2O = CaCl_2 + 2HOCl + CO_2.$$

Hypochlorous acid, being weaker than carbonic acid, cannot decompose a carbonate. $NaHCO_3 + Cl_2 = NaCl + CO_2 + HOCl$.

On a large scale hypochlorous acid is obtained by the action of carbon dioxide upon a suspension of bleaching powder in water.

$$2Ca(OCl)Cl + H_2O + CO_2 = CaCl_2 + CaCO_3 + 2HOCl.$$

Hypochlorous acid is an unstable weak acid and known only in solution—the solution is pale yellow ; stable in the dark, it decomposes on heating or on exposure to light, yielding oxygen and chlorine, and hence a powerful oxidising agent.

$$2HClO = 2HCl + O_2 ; \qquad HCl + HOCl = Cl_2 + H_2O.$$

Hypochlorites.—Hypochlorous acid reacts with alkalis to form hypochlorites. Sodium hypochlorite solution may be obtained by passing chlorine into cold dilute caustic soda solution ; the solution cannot be concentrated, since hypochlorite decomposes into chlorate and chloride. It is manufactured by the electrolysis of cold brine such that the products, chlorine and sodium hydroxide, react yielding hypochlorite. Addition of a little K_2CrO_4 which prevents reduction of hypochlorite by nascent hydrogen, to the electrolytic bath improves the yield.

$$Cl_2 + 2NaOH = NaCl + NaOCl + H_2O.$$

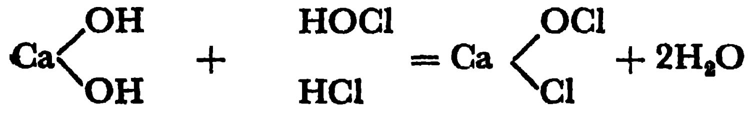
A powerful oxidising agent, it is a valuable disinfectant and bleaching agent. It liberates iodine from potassium iodide—a reaction used for its estimation.

$$NaOCl + 2KI + 2HCl = NaCl + 2KCl + H_2O + I_2.$$

Calcium hypochlorite may be obtained by the action of chlorine upon milk of lime in the cold, and evaporating the solution in vacuum when the crystalline hydrate, $Ca(OCl)_2, 4H_2O$, deposits.

Bleaching powder, Chloride of lime, *Ca(OCl)Cl*.—The most important derivative of hypochlorous acid is bleaching powder, calcium chloro-hypochlorite, Ca(OCl)Cl. This is obtained commercially by the action of chlorine upon slaked lime :

$$Cl_2 + H_2O = HCl + HOCl$$



$$Ca\begin{matrix}OH \\ OH\end{matrix} + \begin{matrix}HOCl \\ HCl\end{matrix} = Ca\begin{matrix}OCl \\ Cl\end{matrix} + 2H_2O$$

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O.$$

Chlorine gas (as obtained by the electrolytic process), free from moisture and carbon dioxide, and generally diluted with air, is passed into a series of lead chambers (typically ten) having concrete floors; slaked lime (containing not more than 4 per cent moisture) is spread on the floor of the chambers to a depth of 3 inches, and this is then furrowed for uniform absorption of chlorine. The process is complete within a day's time, the chambers are *blown out with air* until the atmosphere is sweet, and also dusted with lime to remove the last trace of chlorine. The chambers are then opened and workmen get in and shovel the finished product through ports in the floor into barrels. The temperature is not allowed to rise above 35—40°C. The temperature is controlled by the circulation of cold water through cooling coils embedded in the floors. The product contains about 35—37% available chlorine.

In a continuous process, slaked lime is gradually pushed by mechanical rakes over and down the floors (typically ten) of a cylindrical tower of reinforced concrete and lined, inside with tar and fire clay; chlorine is fed in from the bottom. Chlorine is absorbed by slaked lime on counter-current principle. The finished product is freed from chlorine by a blast of air at the bottom of the cylinder and then discharged into wooden drums. The temperature is controlled by circulating cold water through pipes embedded in the floors.

Bleaching powder is also called chloride of lime.

Properties.—(i) A white powder, smelling strongly of chlorine, bleaching powder absorbs moisture from the air, but is not deliquescent. It does not dissolve completely in water, always leaving a white residue of lime; the aqueous suspension, however, contains the calcium hypochlorite in solution.

(ii) Unstable to heat; the moisture and carbon dioxide of the atmosphere decompose it, liberating chlorine.

$$Ca(OCl)Cl + CO_2 = CaCO_3 + Cl_2.$$

(iii) It reacts with dilute acids to give chlorine:

$$Ca(OCl)Cl + H_2SO_4 = CaSO_4 + H_2O + Cl_2$$

$$Ca(OC)Cl + 2HCl = CaCl_2 + H_2O + Cl_2.$$

The chlorine thus set free is known as **available chlorine** and is responsible for the *bleaching and oxidising properties* of bleaching powder. The valuation of bleaching powder depends upon its content of available chlorine which is expressed as the number of parts by weight of it which may be obtained from 100 parts by weight of the sample by treatment with dilute acids, and is generally spoken of as the "percentage of available chlorine" which is usually 35—37% in a commercial sample.

(iv) Cobalt salts decompose a suspension of bleaching powder catalytically, liberating oxygen: $2Ca(OCl)Cl = 2CaCl_2 + O_2$.

(v) A solution of sodium hypochlorite and chloride is formed by precipitating bleaching powder solution with sodium carbonate:

$$CaOCl_2 + Na_2CO_3 = CaCO_3 + NaOCl + NaCl.$$

(vi) It is a powerful oxidising agent; thus it liberates iodine from an acidified solution of potassium iodide—a reaction made use of for its valuation: $Ca(OCl)Cl + 2KI + 2HCl = CaCl_2 + 2KCl + H_2O + I_2$.

It oxidises sodium arsenite to arsenate—a reaction also used for its valuation.

$$Na_3AsO_3 + CaOCl_2 = Na_3AsO_4 + CaCl_2.$$

Uses.—Bleaching powder is used as a disinfectant, for sterilising water and in the manufacture of chloroform. But its principal use is for bleaching paper-pulp, cotton and linen.

The fabric to be bleached is boiled with dilute caustic soda to remove greasy impurities and then washed with water ; it is next steeped in a solution of bleaching powder and then left exposed to air for several hours when the bleaching is done by chlorine liberated from the bleaching powder by atmospheric carbon dioxide. The fabric is then washed with dilute sulphuric acid to destroy any excess bleaching powder, and finally with sodium sulphite solution to remove the last trace of chlorine.

Bleaching powder with a dilute acid is used for rendering wool unshrinkable.

Bleaching powder is now largely displaced as a bleach by : (i) liquid chlorine, and (ii) calcium hypochlorite, the so-called **high test hypochlorite.** Calcium hypochlorite is made in bulk by chlorination of a lime slurry followed by its separation as crystals by salting out with common salt. The commercial product **Maxochlor** is twice as strong as ordinary bleach and contains 75% available chlorine. It is stable, and does not spoil on keeping, and is completely soluble in water, **perchloron,** calcium hypochlorite stabilised with a little $Ca(OH)_2$, is another high test hypochlorite.

Formula of Bleaching Powder.—Bleaching powder was suggested by Balard (1835) to be a mixture of equimolecular amounts of calcium chloride, and hypochlorite, $CaCl_2 + Ca(OCl)_2$, since its solution gives the tests for both. But the view was rejected because—

(i) bleaching powder is not very deliquescent while any mixture containing calcium chloride should be highly so.

(ii) the alcoholic extract of bleaching powder contains practically no calcium chloride, though the latter is soluble in alcohol.

(iii) moist carbon dioxide liberates the whole of available chlorine from bleaching powder, while it has no action upon calcium chloride.

Odling suggested the formula Ca(OCl)Cl—calcium chloro-hypochlorite for bleaching powder. The formula explains all its reactions and also agrees with its theoretical available chlorine content which is 49.

The formula for bleaching powder, therefore, is : Ca(OCl)Cl. Bleaching powder is now regarded as a mixture of calcium hypochlorite, $Ca(OCl)_2$, $4H_2O$ and basic calcium chloride, $CaCl_2$, $Ca(OH)_2$, H_2O.

Chlorine dioxide.—It is obtained as a yellow gas by cautiously warming to 70° a mixture of powdered potassium chlorate and well-cooled concentrated sulphuric acid.

$$3KClO_3 + 3H_2SO_4 = 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O.$$

An explosive gas, it dissolves in water—the solution is neutral but it reacts with alkali, giving a mixture of chlorite and chlorate.

$$2ClO_2 + 2NaOH = NaClO_2 + NaClO_3 + H_2O.$$

When cooled in freezing mixture the gas condenses to a dark red liquid. A non-explosive mixture of ClO_2 and CO_2 is formed by heating at 60°C a mixture of $KClO_3$ and oxalic acid $H_2C_2O_4$.

$$2HClO_3 + H_2C_2O_4 = 2H_2O + 2ClO_2 + 2CO_2.$$

ClO_2 is prepared pure by passing chlorine over silver chlorate at 90° and condensing the chlorine dioxide as liquid in a freezing mixture.

$$2AgClO_3 + Cl_2 = 2AgCl + 2ClO_2 + O_2.$$

ClO_2 is a powerful oxidising agent. Sodium chlorite is used under the name *textone* as a bleaching agent for paperpulp, cotton and rayon.

Chlorous acid.—It is obtained by the action of dilute sulphuric acid upon barium chlorite and filtering from barium sulphate :

$$Ba(ClO_2)_3 + H_2SO_4 = BaSO_4 + 2HClO_2.$$

Barium chlorite is prepared by passing chlorine dioxide into a suspension of barium peroxide in hydrogen peroxide. $BaO_2 + 2ClO_2 = Ba(ClO_2)_2 + O_2$.

Chloric acid and chlorates.—Chloric acid is prepared by the action of dilute sulphuric acid upon barium chlorate and filtering from the insoluble barium sulphate.

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$

The solution may be concentrated in a vacuum to 40% $HClO_3$; on further concentration or on heating, it decomposes, giving perchloric acid and chlorine dioxide. $3HClO_3 = HClO_4 + 2ClO_2 + H_2O$.

Chlorine hexoxide.—Cl_2O_6 is made by mixing ClO_2 and ozonised oxygen at 0°. It is a dark red liquid. It dissolves in water and forms chlorate and perchlorate with alkali. $Cl_2O_6 + 2KOH = KClO_3 + KClO_4 + H_2O$.

Potassium chlorate, $KClO_3$.—It may be prepared in the following way : Chlorine is passed through an inverted funnel into a hot concentrated caustic potash solution in a beaker. When the solution smells strongly of chlorine, it is cooled and the crystals of potassium chlorate are filtered off, washed with cold water and finally recrystallised from hot water.

Potassium chlorate is obtained commercially by—(i) **Chemical method.**—Calcium chlorate is made by bubbling chlorine into hot milk of lime contained in cast-iron vats with agitating paddles ; powdered potassium chloride is then added to the calcium chlorate liquor, when the sparingly soluble (solubility, 5.7% at 15°) potassium chlorate separates on cooling. The crude product is recrystallised from hot water.

$$6Ca(OH)_2 + 6Cl_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O.$$
$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3.$$
$$3Cl_2 + 6KOH = KClO_3 + 5KCl + 3H_2O.$$

(ii) **Electrolytic method.**—Sodium chlorate is prepared by electrolysing common salt in such a way that the products of electrolysis at the anode and the cathode are allowed to mix freely. A hot (85°—90°C) saturated solution of common salt, to which a little *free* acid (about 5 gms. HCl per litre) and sodium dichromate (about 2 gms. per litre) have been added, is electrolysed between *iron cathodes* and *smooth platinum anodes*—the liquor being contained in a lead-lined steel cell. The sodium chloride on electrolysis yields chlorine, caustic soda and hydrogen. The chlorine liberated at the anode reacts with caustic soda formed at the cathode—hydrogen evolved at the cathode passes out—yielding sodium hypochlorite. The hypochlorite is then oxidised to chlorate by hypochlorous acid which is always present in the liquor owing to the *acidity* of the bath. The addition of dichromate prevents cathodic reduction of the chlorate.

$$Cl_2 + 2NaOH = NaCl + NaOCl + H_2O \text{ ;}$$
$$2HClO + NaOCl = NaClO_3 + 2HCl.$$

The electrolysed solution is then concentrated when the less soluble sodium chloride is first deposited which is filtered off—the mother liquor containing the more soluble sodium chlorate is then crystallised for the latter. Potassium chlorate is obtained by treating a solution of sodium chlorate with potassium chloride, when the sparingly soluble potassium chlorate crystallises out :

$$NaClO_3 + KCl = KClO_3 + NaCl.$$

Potassium chlorate may also be made by the electroysis of potassium chloride solution—the sparingly soluble potassium chlorate crystallising out.

Properties.—(i) A white crystalline solid, sparingly soluble in water potassium chlorate melts at 370°. Sodium chlorate is very soluble in water.

(ii) Heated just above its melting point 370°, it is converted into a mixture of potassium chloride and oxygen :

$$4KClO_3 = KCl + 3KClO_4 \; ; \; KClO_4 = KCl + 2O_2.$$

Heated with manganese dioxide, potassium chlorate decomposes below its melting point into potassium chloride and oxygen—no perchlorate is formed.

(iii) Chlorates are powerful oxidising agents ; it is reduced by hot sulphurous acid to chloride which yields a white precipitate with silver nitrate—the chlorate is not precipitated by silver nitrate.

$$KClO_3 + 3H_2SO_3 = KCl + 3H_2SO_4.$$

(v) It oxidises hot concentrated hydrochloric acid to yellow **euchlorine gas**, a mixture of Cl_2 and ClO_2.

$$2KClO_3 + 4HCl = 2KCl + Cl_2 + 2ClO_2 + 2H_2O.$$

(v) It reacts with concentrated sulphuric acid, yielding the explosive gas chlorine dioxide and perchloric acid.

$$3KClO_2 + 3H_2SO_4 = 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O.$$

Uses.—Potassium chlorate forms dangerous explosive mixtures with sulphur, phosphorus and charcoal and hence its use as an ingredient in fire-works and matches ; mixed with magnesium and red phosphorus, it is also used in photographic flash powders ; also as an oxidising agent : It is used in medicine as an antiseptic in the form of chlorate lozenges for the cure of sore throats.

On adding conc. H_2SO_4 by means of a pipette into a mixture of potassium chlorate and sugar taken on an asbestos board, the sugar bursts into flame and is converted into black mass of charcoal—the reaction is caused by the action of sugar upon chlroine dioxide formed.

Perchloric acid, $HClO_4$ is formed by the decomposition of chloric acid on distillation : $3HClO_3 = HClO_4 + Cl_2 + 2O_2 + H_2O$.

It is usually prepared by distilling potassium perchlorate with concentrated sulphuric acid in a retort—the perchloric acid collects in the receiver as a colourless fuming liquid which gradually solidifies to the monohydrate $HClO_4,H_2O$, m.p. 50°. The anhydrous perchloric acid is obtained by distillation under reduced pressure as a colourless mobile liquid. It is the most stable oxy-acid of chlorine ; it may explode when heated at atmospheric pressure. It is a strong acid. It is an oxidising agent and inflames paper and wood. Perchloric acid is used for the gravimetric estimation of potassium as potassium perchlorate.

$$KClO_4 + H_2SO_4 = KHSO_4 + HClO_4.$$

Potassium perchlorate, $KClO_4$.—It is prepared by heating potassium chlorate

$$4KClO_3 = 3KClO_4 + KCl.$$

Potassium chlorate is heated in a porcelain dish until the fused salt becomes pasty. The cold mass is ground with cold water in a mortar for separating the chloride—the residual perchlorate is then crystallised from hot water. Any chlorate remaining may be decomposed by boiling with a little concentrated hydrochloric acid, which does not act upon the perchlorate ; the potassium perchlorate is filtered, and recrystallised from hot water.

$KClO_4$ is sparingly soluble in water. It decomposes at a higher temperature than the chlorate : $KClO_4 = KCl + 2O_2$. It does not bleach indigo in presence of sulphite as does the chlorate. With hot concentrated sulphuric acid it gives fumes of perchloric acid, while the chlorate yields the explosive gas ClO_2. It is not acted upon by hot and strong HCl which decomposes the chlorate, giving off *euchlorine, vide supra.*

Sodium perchlorate is deliquescent and very soluble in water. Silver perchlorate is soluble in water and toluene. Magnesium perchlorate is a good drying agent. Perchlorates are used to make detonators and explosives.

Chlorine Heptoxide, Cl_2O_7, is the anhydride of perchloric acid. It is a colourless explosive liquid. It slowly forms perchloric acid with water :

$$Cl_2O_7 + H_2O = 2HClO_4.$$

It is obtained by dehydrating anhydrous perchloric acid with phosphorus pentoxide at −10°C and very carefully distilling from a retort.

Oxides and oxyacids of bromine and iodine

Oxides of Bromine.—Three oxides of bromine Br_2O, BrO_2 and BrO_3 are known. BrO_3 is formed as a white crystalline solid, stable only below—80°, by oxidising bromine vapour with pure ozone at 0° under a low pressure. Bromine monoxide, Br_2O, is formed when bromine reacts with dry mercuric oxide. It readily decomposes.

Oxides of Iodine.—Iodine Pentoxide.—I_2O_5, is obtained as a white powder by heating iodic acid to 200°. It dissolves in water to form iodic acid :

$2HIO_3 \leftrightharpoons I_2O_5 + H_2O$. It oxidises carbon monoxide, even if present in traces only, on warming : $5CO + I_2O_5 = 5CO_2 + I_2$.

Iodine Tetroxide, I_2O_4, is obtained as a yellow powder by the action of cold nitric acid upon iodine or by heating iodic acid with concentrated sulphuric acid. It decomposes into iodine and iodine pentoxide at 180°. I_4O_9 is formed by the action of ozonised oxygen on iodine.

Bromine forms the oxyacids : *hypobromous acid,* HOBr, *bromous acid,* $HBrO_2$ and *bromic acid,* $HBrO_3$, all known only in solution.

The oxyacids of iodine are *hypoiodous acid,* HOI ; *iodic acid,* HIO_3 ; *periodic acid,* HIO_4, $2H_2O$ or H_5IO_6.

Hypobromous and Hypoiodous Acids.—An aqueous straw-yellow solution of hypobromous acid is obtained by shaking bromine water with yellow mercuric oxide and filtering. The solution is an oxidising and bleaching agent :

$$2Br_2 + 2HgO + H_2O = HgO, HgBr_2 + 2HOBr.$$

The hypoiodous acid is prepared similarly.

A mixture of hypobromite and bromide is obtained by treating cold aqueous soda and potash with bromine. The hypo-bromite in solution changes to bromate on keeping or warming :

$$Br_2 + 2NaOH = NaOBr + NaBr + H_2O \ ; \quad 3NaOBr = NaBrO_3 + 2NaBr.$$

The hypoiodite resembles hypobromite but is less stable. It is prepared similarly. The stability of the acids of type HOCl diminishes from chlorine to iodine.

Bromic and Iodic acids.—Bromic acid, $HBrO_3$, is obtained in solution by treating silver bromate, precipitated by adding silver nitrate to a solution of potassium bromate, with bromine water and filtering :

$$5AgBrO_3 + 3Br_2 + 3H_2O = 5AgBr + 6HBrO_3.$$

The solution may be concentrated in *vacuo* but decomposes to bromine and oxygen on heating : $4HBrO_3 = 2Br_2 + 5O_2 + 2H_2O$. The solution has oxidising properties : $2HBrO_3 + 5SO_2 + 4H_2O = Br_2 + 5H_2SO_4$.

$$2HBrO_3 + 5H_2S = Br_2 + 6H_2O + 5S \ ; \ HBrO_3 + 5HBr = 3Br_2 + 3H_2O.$$

A bromide-bromate mixture on acidification liberates bromine and is used for analytical purposes.

$$5KBr + KBrO_3 + 6HCl = 6KCl + 3H_2O + 3Br_2.$$

Iodic Acid, HIO_3, is prepared by boiling iodine with concentrated nitric acid. The liquid is evaporated to dryness and heated to 200° to expel the nitric acid. The residue of iodine pentoxide is dissolved in minimum quantity of water and left to crystallise, when colourless crystals separate :

$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O.$$

It may also be obtained by the action of chlorine on a suspension of iodine in water : $I_2 + 5Cl_2 + 6H_2O = 10HCl + 2HIO_3$, also by evaporating iodine with chloric acid : $2HClO_3 + I_2 = 2HIO_3 + Cl_2$.

At 200° iodic acid yields the anhydride I_2O_5, which decomposes to iodine and oxygen at 300°. An oxidising agent, iodic acid resembles bromic acid in oxidising actions. Although monobasic, iodic acid forms normal and acid salts, e.g., KIO_3, and acid potassium iodate, also called potassium bi-iodate, $KH(IO_3)_2$.

Potassium Bromate, $KBrO_3$, may be made by dissolving bromine in hot concentrated potassium hydroxide solution :

$$3Br_2 + 6KOH = 5KBr + KBrO_3 + 3H_2O.$$

It is *sparingly soluble* and is separated from the potassium chloride by crystallisation. Potassium bromate decomposes to potassium bromide and oxygen when heated :

$$2KBrO_3 = 2KBr + 3O_2 \text{ (cf. } KClO_3).$$

Potassium Iodate. KIO_3, is sparingly soluble ; it resembles potassium bromate and is prepared similarly, *vide supra.* It is best made by heating potassium chlorate solution with iodine : $2KClO_3 + I_2 = 2KIO_3 + Cl_2$. An iodate-iodide mixture liberates iodine on acidification : $5KI + KIO_3 + 6HCl = 6KCl + 3H_2O + 3I_2$.

Periodic Acid.—Periodic acid, H_5IO_6, and potassium periodate, KIO_4, are prepared by the electrolytic oxidation of iodic acid and potassium iodate respectively. Iodic acid solution is taken in a porous pot in which is placed the anode—a lead plate coated with lead peroxide ; the pot stands in dilute sulphuric acid in which is dipped a platinum cathode—the electrolysed solution in the porous pot yields periodic acid on crystallisation. Sparingly soluble potassium periodate is obtained by electrolysing potassium iodate in the same way. Periodate is also made by oxidising an iodate in alkaline solution by chlorine. The acid forms colourless, deliquescent crystals which melt at 133° and decomposes at 140° ; $2H_5IO_6 = I_2O_5 + 5H_2O + O_2$. *The acid is pentabasic* and hence the formula H_5IO_6. The solution is strongly acid and is an oxidising agent. Periodic acid and its salts are more stable than their chlorine analogues. Barium periodate is formed by heating barium iodate to redness :

$$5Ba(IO_3)_2 = Ba_5(IO_6)_2 + 4I_2 + 9O_2.$$

Perbromic acid is unknown.

Comparison of the Properties of Halogens.—The halogens fluorine, chlorine, bromine, and iodine, which belong to group VIIb in the periodic table form a family of closely related elements. Their properties show a regular gradation with increasing atomic weights from fluorine to iodine, as the table of their properties most convicingly illustrates :

The halogens do not occur in the free state. They are monovalent and form univalent anions in their halides, e.g., NaF, NaCl, NaBr and NaI.

(i) The melting and boiling points of the halogens gradually increase from fluorine to iodine with increasing atomic weight ; the state of existence of the halogens shows a gradation from gas to solid with deepening of colour—their density, also increasing with increasing atomic weight.

(ii) The halogens are the **most electro-negative** (non-metallic) elements—the non-metallic character gradually decreasing from fluorine to iodine. As non-metals, they exhibit great **affinity for hydrogen and metals,**—the affinity, however, gradually decreasing from fluorine to iodine, as the reactions of the halogens with hydrogen, water and metals indicate.

(iii) The halogens are very reactive chemically. The *reactivity* decreases (as their reactions with both metals and non-metals illustrate) in general with decreasing electro-negativeness ; thus fluorine can displace chlorine from its salts, chlorine can displace bromine, and bromine can displace iodine.

Oxidising and bleaching action.—The halogens are powerful oxidising agents and hence all react with reducing agents—their oxidising power diminishing with decreasing electro-negativeness. The bleaching property decreases from chlorine to iodine which does not bleach at all—fluorine destroys the material to be bleached.

(v) **Affinity for oxygen.**—The affinity for oxygen (unlike that for hydrogen) increases from fluorine to iodine (except in the case of bromine which resembles fluorine in having little affinity for oxygen). Except iodine which is oxidised to iodic acid by hot concentrated nitric acid, the halogens are not affected by oxidising agent—bromine however forms an unstable oxide with ozone. A large number of oxides of halogens have been obtained by *indirect means*.

The stability of the oxyacids also increases from chlorine to iodine (Bromate is less stable than chlorate, and fluorine forms no oxyacid) ; thus iodine liberates chlorine from potassium chlorate. $2KClO_3 + I_2 = 2KIO_3 + Cl_2$.

(vi) **Action of alkali.**—Fluorine differs from other halogens in not forming oxysalts with alkalis—with cold dilute alkali, it reacts, yielding fluorine monoxide, F_2O, while with hot concentrated alkali oxygen is liberated. Chlorine, on the other hand, reacts with cold dilute alkali, producing chloride and hypo-chlorite ; with hot concentrated alkali it yields chloride and chlorate. Bromine and iodine behave like chlorine.

Hydrides of Halogens, Comparison of,—(i) The halogen hydrides are colourless gases (HF is a liquid below 19.5° which fumes strongly in moist air). HF is highly poisonous. The gases, all heavier than air except HF which is lighter, do not burn nor support burning ; they exhibit a gradation in properties except HF whose abnormal behaviour is due to the association of its molecules :

(ii) The stability of the hydrides decreases from HF to HI, as the effect of heat upon them clearly indicates.

(iii) **Effect of oxidising Agents.**—The ease of oxidation increases with the decrease of the stability of the hydrides ; HF is not affected by oxidising agents ; HCl is oxidised to chlorine and water by strong oxidising agents, such as permanganate, dichromate, nitric acid, manganese dioxide, etc. ; besides by those mentioned under HCl, HBr is also oxidised to bromine and water by hydrogen peroxide, chlorine and concentrated H_2SO_4 ; HI is readily oxidised to iodine and water by all oxidising agents, including the above, and also by cupric and ferric salts and nitrous acid. HI is so easily oxidised that it is frequently used as a reducing agent.

(iv) **Strength of acid.**—Hydrogen fluoride is a much weaker acid than HCl, HBr and HI which are equally strong. HF differs from other hydracids in etching glass. Hydrofluoric acid is *associated* at low temperature ; it is H_2F_2 in concentrated solution.

(v) **Halides.**—Calcium fluoride is insoluble in water, while the corresponding chloride, bromide, and iodide are soluble in water. Silver fluoride, on the other hand, is soluble in water, whilst the chloride, bromide and iodide are insoluble.

Comparison of the Properties of halogens

Physical properties	*Fluorine*	*Chlorine*	*Bromine*	*Iodine*
(i) Atomic number	9	17	35	53
(ii) Atomic weight	19	35.457	79.916	126.91
(iii) Colour and form	Pale yellow gas	Greenish yellow gas	Dark red liquid ; gives off red vapours	Grey lustrous solid ; gives off violet vapours on heating
(iv) Smell	Irritating	Irritating	Extremely irritating	Irritating smell of vapour
(v) Specific gravity	1.11 (liquid at boiling point)	1.55 (liquid at boiling point)	3.19 (liquid at 0°C)	4.94 (solid at 18°C)
(vi) Melting point °C	−223°	−102°	− 7°	+114°
(vii) Boiling point	−187°	− 34°	+59°	+184°
(viii) Solubility in water at 0°	Decomposes water	14.6 gms. per litre	41.5 gms. per litre	0.162 gm. per litre
Chemical properties				
(i) Whether combustible or not	Fluorine inflames in hydrogen, otherwise non-combustible	Chlorine burns in hydrogen, otherwise non-combustible	Non-combustible	Non-combustible
(ii) If supporter of combustion	As, S, P, Na, K, etc. spontaneously catch fire in the gas, forming their fluorides.	As, Sb, P, Cu, etc. spontaneously ignite in the gas. Heated sodium also burns in the gas.	As, Sb, P, etc. spontaneously burn in the bromine vapours	Iodine vapours support combustion of As, Sb, P etc. ; but less energetically
(iii) Reaction with hydrogen. Affinity for H_2 decreases from F_2 to I_2	Explosive even in the dark, forms HF even at −252°.	Explosive in sunlight ; froms HCl ; no reaction in the dark	Forms HBr in contact with heated platinum	Slowly forms HI in contact with heated platinum
(vi) Action on metals, forming halides	Attacks all metals—most metals burn, e.g., Na, K.	Attacks all metals—many metals burn, e.g., Na	Attacks most metals—a few only burn, e.g. K.	Attacks most metals except platinum.
(v) Action on non-metals, forming halides.	Combines directly with all except N_2 and O_2.	Combines directly with all except C, N_2 and O_2.	Combines directly with all except C, Si, N_2 and O_2.	Combines directly with halogens, hydrogen, P and As.

Chemical properties	*Fluorine*	*Chlorine*	*Bromine*	*Iodine*
(vi) Action on water	Decomposes water, forming HF, O_2 and a little ozone.	Dissolves to form chlorine water, which evolves O_2 in sunlight : $Cl_2+H_2O=HCl+HOCl$ $=2HCl+O$ Also directly decomposes water in sunlight : $Cl_2+H_2O \rightleftharpoons 2HCl+O$	More soluble than Cl_2 ; bromine water slowly liberates O_2 in sunlight $Br_2+H_2O=2HBr+O$	Slightly soluble in water. Freely soluble in water containing KI in solution.
(vii) Reactivity ; reactivity decreases from F_2 to I_2	Most reactive ; liberates Cl, Br, and I respectively from HCl, HBr, HI and their salts.	Less reactive than fluorine ; liberates Br and I respectively from HBr, HI and their salts	Less reactive than chlorine ; liberates iodine from HI and its salts	Least reactive, cannot liberate F, Cl, and Br from HF, HCl, HBr and their salts.
(viii) Reaction with caustic alkali : (a) Cold solution	(a) Forms F_2O with cold dilute alkali but evolves O_2 with concentrated alkali.	(a) Forms chloride and *hypochlorite*	(a) Forms bromide and *hypobromite*	(a) Forms iodide and *hypoiodite*
(b) Hot solution	(b) *No oxyacids and oxy salts are formed.*	(b) Forms chloride and *chlorate*	(b) Forms bromide and *bromate*	(b) Forms iodide and *iodate*
(ix) Oxidising action	Vigorous oxidising agent	Strong oxidising agent $H_2S+Cl_2=2HCl+S$	Oxidising agent $H_2S+Br_2=2HBr+S$	Feeble oxidising agent $H_2S+I_2=2HI+S$
(x) Bleaching action	Destroys the material	Readily bleaches in presence of moisture	Slowly bleaches in presence of moisture	No bleaching action
(xi) Action on starch solution	Attacks the solution	No change of colour	Yellow coloration	Blue coloration
(xii) Action of oxidising agent	- No action Indirectly forms F_2O and F_2O_2	No action Indirectly forms Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7	Oxidised to BrO_3 by ozone. Indirectly forms Br_2O and BrO_3	Oxidised by ozone and also by nitric acid to iodic acid. Forms the oxides I_2O_4, I_2O_5 and I_4O_9

The properties of hydrides of halogens :—

Properties	HF	HCl	HBr	HI
(i) State at 15°	Colourless Liquid	Colourless Gas	Colourless Gas	Colourless Gas
(ii) Melting point	−83°C	−114°C	−87°C	−51°C
(iii) Boiling point	19.5°C	− 85°C	−67°C	−35°C
(iv) Solubility in water at 0°	Miscible	500 volumes 42 per cent	600 volumes 68 per cent	70 per cent
(v) Heat of formation	+64,200 calories	+22,063 calories	+8,660 calories	−6,200 calories
(vi) Effect of heat	Nil	Dissociation at 1500°C	Dissociation at 800°C	Dissociation in sun light and at 180°C
(vii) Constant boiling mixture : (*a*) b.p.	120°C	110°C	125°C	127°C
(*b*) composition	35 per cent HF	20 per cent HCl	48 per cent HBr	58 per cent HI
(viii) Action of oxidising agents	No action	Oxidised to Cl_2 by MnO_2, $KMnO_4$, HNO_3, $K_2Cr_2O_7$ chlorate and perchlorate.	Oxidised to Br_2 as with Cl_2 and also by H_2SO_4, H_2O_2 and chlorine.	Oxidised to I_2 by most oxidising agents including HNO_2, cupric and ferric salts.
(ix) Strength of acid	Fairly weak acid ; forms acid salts.	Strong acid	Strong acid	Strong acid
(x) Solubility of halides in water	AgF soluble ; CaF_2 insoluble Hydrogen fluoride is an associated liquid ; it etches glass	AgCl insoluble $CaCl_2$ soluble	AgBr insoluble $CaBr_2$ soluble	AgI insoluble CaI_2 soluble

Distinctive tests of halides :—

Tests	Fluoride	Chloride	Bromide	Iodide
A little solid halide : (i) heated with concentrated H_2SO_4	White fumes of HF which *etch* glass.	White fumes of HCl ; do not etch glass ; give dense white fumes with ammonia.	Red vapours of bromine.	Violet vapours of iodine.
(ii) heated with MnO_2 and concentrated H_2SO_4	No fluorine is liberated.	Greenish yellow Cl_2 which turns starch-iodide paper blue.	Red bromine vapours which turn starch iodide paper blue.	Violet iodine vapours which turn starch blue.
An aqueous solution of the halide :				
(a) treated with $AgNO_3$ solution	No precipitate	Curdy white ppt. of AgCl, insoluble in HNO_3 but soluble in ammonia.	Pale yellow ppt. of AgBr, insoluble in HNO_3 but difficultly soluble in ammonia.	Yellow precipitate of AgI, insoluble in HNO_3, and also in ammonia.
(b) shaken with chlorine water and CS_2	No coloration	No coloration	Orange-red CS_2-layer.	Violet CS_2-layer.
(c) shaken with chlorine water and then starch solution added.	No coloration	No coloration	Orange-yellow colour.	Blue colour.

Exercises

1. How was fluorine isolated ? Give reasons for the procedure adopted. Compare its properties with those of chlorine. *Calcutta '54*

2. Name two minerals of fluorine. How is anhydrous hydro-fluoric acid prepared ? What is meant by etching of glass ? Compare the properties of the hydracids of the halogens. *Punjab '27*

3. Describe the preparation of a sample of chlorine free from hydrogen chloride. Explain, with equations, the action of chlorine upon—(*a*) milk of lime, (*b*) sulphurous acid, (*c*) hydrogen sulphide, (*d*) molten tin, (*e*) chalk in suspension in water, (*f*) quick lime. *Patna Inter.*

4. Describe how (*a*) a solution of potassium hydroxide, (*b*) a solution containing a hypochlorite, (*c*) crystals of potassium chlorate, may be obtained as direct results of electrolysis of potassium chloride solution.

A few grams of potassium got mixed up with mercury. The mixture was treated with water and the aqueous solution was then separated, warmed and then allowed to be mixed up with a stream of chlorine gas. When the solution was almost saturated with chlorine, a crystalline product separated out. This was filtered and kept at 370° for some time. This was then crystallised from hot water. What was the final product ? *Potassium perchlorate, Calcutta '41*

5. How is bleaching powder manufactured ? What is its formula ? What is meant by the term 'available chlorine' of a sample of bleaching powder ? How would you proceed to bleach a fabric with it ? How may oxygen be obtained from bleaching powder ? *Ajmer Inter. '33*

In alkali factory chlorine is a by-product. How can this be best utilised ?

6. What is the chief source of bromine and how is it obtained in the pure state ? How may specimens of (*a*) hydrogen bromide, (*b*) potassium bromide be prepared from bromine ? Describe the reactions of bromine with (*i*) phosphorus, (*ii*) sulphur dioxide, (*iii*) sodium carbonate and (*iv*) potassium iodide. *Bombay '53*

7. What are the chief sources of iodine ? Indicate the reactions by which it is obtained from them. Describe and explain the actions of iodine on (*a*) mercury, (*b*) nitric acid, (*c*) sodium thiosulphate, (*d*) hydrogen sulphide, (*e*) potassium iodide, (*f*) caustic soda, (*g*) iron filings. *Cal. '57, Madras '49*

8. How is hydrochloric acid obtained commercially and for what purposes is it used ? How would you establish that its formula is HCl ? How would you detect traces of chlorine in hydrochloric acid ?

9. How are (*a*) hydrogen chloride and (*b*) hydrogen iodide usually prepared in the laboratory ? Comment on the different methods employed. What happens when their aqueous solutions are treated with (*i*) silver nitrate in excess of ammonia, (*ii*) copper sulphate, (*iii*) ferric chloride solution ? How would you distinguish iodides from chlorides and bromides ? *Patna Inter.*

10. Compare the properties of the halogens and their hydracids and justify their inclusion in the same group in the periodic table.

In what respects do fluorine and chlorine and also their compounds differ from one another ?

11. Describe the action of concentrated sulphuric acid on potassium chloride, potassium bromide, and potassium iodide. State briefly how you would prepare specimens of each of the following acids : hydrochloric, hydrobromic, hydriodic. Give equations representing the reaction. By what tests would you distinguish and identify hydrobromic and hydriodic acid solutions ? *Calcutta '53*

Explain what happens when : (*a*) a heated glass rod is inserted in a jar of hydriodic acid.

(*b*) hydriodic acid is led into copper sulphate solution.

(*c*) an aqueous solution of hydriodic acid is exposed to air for some time.

12. Iodine resembles graphite in appearance. How would you distinguish between them ? Explain how you would separate a mixture of iodine and potassium iodide.

Describe what happens when : (*a*) a crystal of iodine is heated in a flask.

(*b*) chlorine water is added to potassium iodide solution, and then shaken with carbon disulphide.

(*c*) a mixture of potassium iodide and iodate is acidified.

(*d*) a crystal of iodine is shaken with potassium iodide solution.

(*e*) iodine is heated with concentrated nitric acid.

(*f*) chlorine acts on a suspension of iodine in water.

13. Describe the preparation of a specimen of hydrobromic acid. How would you obtain an aqueous solution of hydrobromic acid from bromine water, and *vice versa* ? Compare the properties of hydrobromic acid with those of hydrochloric and hydriodic acids. *Calcutta '47*

14. Some iodine got mixed with potassium iodide. How will you separate them ?

Discuss the chemical changes that take place when (a) iodine is mixed with caustic soda solution, (b) potassium iodide is mixed with concentrated sulphuric acid, (c) gaseous chlorine is passed into aqueous solution of potassium iodide, (d) potassium iodide is added to mercuric chloride solution. *Calcutta '47*

15. How is hydriodic acid prepared in laboratory ? Give a neat sketch of the apparatus used. Compare its properties with those of hydrochloric acid. *Punjab '49*

Describe the changes that occur when (*a*) gaseous hydriodic acid is heated (*b*) when its aqueous solution is treated successively with silver nitrate and ammonia, (*c*) when chlorine is passed into its solution followed by hydrogen sulphide. *Calcutta '45*

16. Explain how chlorine bleaches. Give examples to illustrate it. Describe the action of chlorine with (*a*) oil of turpentine, (*b*) aqueous solution of ferrous chloride, (*c*) hot caustic potash solution, (*d*) a solution of potassium iodide, (*e*) hydrogen, (*f*) heated iron wire, and (*g*) water. How would you know that sodium chloride contains chlorine ?

17. Explain what happens when : (*i*) a jet of burning hydrogen is introduced into a jar of chlorine, (*ii*) dry chlorine is passed over molten tin, (*iii*) chlorine is passed into ferrous sulphate acidified with sulphuric acid, (*iv*) an aqueous solution of chlorine is exposed to sunlight, (*v*) a mixture of hydrogen and chlorine is exposed to sunlight, (*vi*) chlorine is led into a suspension of yellow mercuric oxide, (*vii*) chlorine is passed into hot caustic potash solution until saturated, (*viii*) common salt is heated with manganese dioxide and sulphuric acid, (*ix*) chlorine is led into a jar containing molten phosphorus under water, (*x*) potassium chlorate is warmed with iodine. How would you show that hydriodic acid is a more powerful reducing agent than hydrobromic acid ?

18. Explain what happens when : (*i*) calcium fluoride is heated with concentrated sulphuric acid in a glass test tube, (*ii*) an aqueous solution of hydrofluoric acid is electrolysed, (*iii*) fluorine is led into a cold dilute solution of caustic soda, (*iv*) a suspension of bleaching powder is treated with sodium carbonate solution, (*v*) potassium chlorate is heated with concentrated hydrochloric acid. How would you detect the presence of both a bromide and a chloride in a mixture of the two ?

19. What are the common sources of bromine ? How is bromine manufactured industrially ? State its properties and uses. Name an important bromide and state its uses. *Calcutta '59*

How would you distinguish between : (*i*) nitrogen peroxide and bromine vapour ?

20. Describe the preparation and uses of : (*a*) bleaching powder, (*b*) potassium chlorate. *U. P. Board '51*

XXII

SULPHUR AND ITS COMPOUNDS

	At. wt.	At. no.	Density (solid)	At. vol.	M. pt.	B. pt	Atomicity
Oxygen	16.00	8	1.4	11.2	−218.4°	−184°	O_2
Sulphur	32.06	16	2.1	15.3	112.8°	444.6°	S_8

Electronic configuration ; Oxygen 2, 6 ; Sulphur 2, 8, 6. Oxygen, sulphur, selenium and tellurium belong to group VIb in the periodic table. These elements are classed as non-metals, but there is a gradual increase in the electropositive character with increasing atomic weight.

The properties of oxygen and its compounds *differ* in many respects from those of sulphur—their chief points of difference are :

(i) Oxygen is a gas, while sulphur is a solid at ordinary temperature ; the molecule of sulphur is S_8 but that of oxygen O_2.

(ii) Oxygen is a supporter of combustion, but sulphur is a combustible solid.

(iii) Valency of oxygen is 2, but the maximum valency of sulphur is 6, as in SF_6 but lower valencies of 2 and 4 (as in SO_2) are also shown. Oxygen forms no compounds similar to sulphites and sulphates.

(iv) Hydrogen sulphide H_2S, is a weak acid, whereas water H_2O is neutral.

(v) Water is an associated liquid, mainly a trimer $(H_2O)_3$, at the ordinary temperature, while hydrogen sulphide is a gas consisting of simple molecules of H_2S.

(vi) Chlorides of oxygen, viz., Cl_2O_7, are explosive ; they react with water forming acids, $Cl_2O_7 + H_2O = 2HClO_4$, chlorides of sulphur are not explosive—they are hydrolysed by water, forming HCl and sulphur.

But the chemistry of oxygen and sulphur exhibit some similarity, justifying their placing in the same group :

(a) Both oxygen and sulphur contain 6 electrons in the outermost shell of their atoms, and accordingly form the bicovalent compounds H-O-H and H-S-H, and the bi-electrovalent compounds $Na^+O''Na^+$ and $Na^+S''Na^+$.

(b) Oxides and sulphides show great similarities in their reactions :

$$FeO + 2HCl = FeCl_2 + H_2O \; ; \; FeS + 2HCl = FeCl_2 + H_2S$$

Sulphur may take the position of oxygen in many oxides and oxyacids ; e.g., CS_2 is analogous to CO_2 ; CS_2 reacts with NaOH to form sodium thiocarbonate Na_2CS_3, while CO_2 gives Na_2CO_3 with caustic soda.

SnO_2 is analgous to SnS_2, the former reacts with NaOH to form stannate Na_2SnO_3, while the latter with alkali gives stannate and analogous thiostannate Na_2SnS_3. Both oxygen and sulphur are found free in nature and both exhibit allotropy.

Sulphur

History and Occurrence.—From its occurrence in the free state in Sicily, sulphur or brimstone was known to the ancient Greeks and Romans. The Egyptians were also familiar with it. Homer (900 B.C.) mentions the use of burning sulphur in fumigation, and the fumes thereof were used in the bleaching of textile fabrics at an early date. The use of sulphur in medicine is also a very old practice.

Huge deposits of sulphur occurs in the volcanic regions of Sicily, Japan, and in Louisiana and Texas in U.S.A.—*80 per cent of the total sulphur used in the world is produced in America.*

Sulphur is formed in volcanic districts by interaction between hydrogen sulphide and sulphur dioxide which are present in volcanic gases : $2H_2S + SO_2 = 2H_2O + 3S$.

Combined sulphur occurs as metallic sulphide and *sulphates* ; the more important sulphides are : *galena*, PbS ; *zinc blende*, ZnS ; *copper pyrites*, Cu_2S, Fe_2S_3 ; *cinnaber*, HgS ; and *iron pyrites*, FeS_2. The sulphates are : *gypsum*, $CaSO_4$, $2HO$; *anhydrite*, $CaSO_4$; *heavy spar*, $BaSO_4$ and *kieserite*, $MgSO_4$, H_2O.

Sulphur occurs in many organic matter, for example, in hair, egg albumen, in the odorous principles of garlic, onion and mustard.

Deposits of sulphur occur at Koh-i-Sultan in Beluchistan. Gypsum is found in India.

Extraction of native sulphur.—(a) **Sicilian Sulphur :** Sulphur-bearing rocks, as dug in Sicily, contain about 20 per cent sulphur, besides many impurities such as clay, limestone, sand and gypsum. The sulphur is separated from the rock by *liquation.* The rock is heaped in lumps in brick kilns (called *calcaroni*) built on sloping hillsides, with air spaces, and kindled at the top.

A portion of the sulphur burns, heating the remainder which melts and flows down the floor of the kiln into wooden moulds. The crude sulphur still contains about 5% rocky impurities. About 30% of the sulphur is used up as a fuel.

The process, therefore, appears to be wasteful, but native sulphur is cheaper than imported coal.

The efficiency of the process is increased by using the **Gill Kiln** which consists of a number of communicating brick chambers arranged in a circle ; the hot gases from one chamber in which sulphur has melted passes into the adjoining one and melts out the sulphur there, and thereby economise heat. The recovery of sulphur is about 75 per cent.

The crude sulphur is **refined** at Marseilles, where fuel is cheaper. The sulphur is melted in an iron pot, whence it runs into an iron retort, heated over a coal fire—the sulphur boils, and the vapour is led into a brick-chamber where it condenses on the cold walls as a yellow solid, called **flowers of sulphur.** As the walls become hot, liquid sulphur collects to the bottom, when it is tapped out and cast into wooden moulds to form **roll sulphur** or **brimstone** (fig. 115).

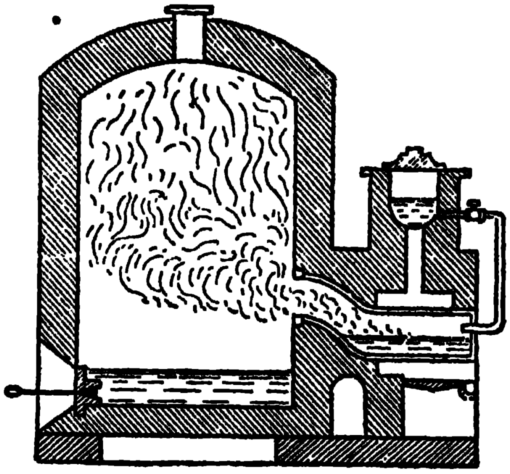


Fig. 115

(b) **American sulphur.**—The deposit of free sulphur in Louisiana and Texas occurs below layers of clay, quicksand and limestone, several hundred feet beneath the surface of the earth and is extracted by the **Frasch process.** A boring is made to the deposit, and 'pump' of four concentric pipes (fig. 116) are sunk to the sulphur-bearing strata—down the two of outer pipes is pumped superheated water at 160° and at a pressure of 10—18 atmospheres, to melt the sulphur. Compressed air at 35 atmospheres is forced down the inner pipe, when a froth of molten sulphur and air bubbles rises to the surface through the remaining pipe. The sulphur is led into wooden vats where it solidifies. It is of 99.5 to 99.9 per cent purity and is ready for immediate use.

Recovered Sulphur.—Important sources are : (*i*) **Coal gas :** Hydrogen sulphide distilled from coal (which contains iron pyrites, FeS_2) in the manufacture of coal gas, *which is recovered as sulphur* from the *spent iron oxide.*

(*ii*) **Sulphide ores :** Sulphur dioxide in the waste gases from the roasting of sulphide ores of copper, lead, nickel and zinc, and from the burning of coal, which is conentrated by absorption in a cold solution containing basic aluminium sulphate or sodium sulphite—the solution on warming evolves sulphur dioxide which is reduced by coke at 1100°C, yielding sulphur :

$$Na_2SO_3 + H_2O + SO_2 \rightleftharpoons 2NaHSO_3$$

$$SO_2 + C = CO_2 + S$$

(*iii*) **Gypsum :** On being heated with sand, clay and coke, gypsum yields sulphur dioxide which is reduced with white-hot coke at 1100°, as above.

(*iv*) **Alkali waste :** Sulphur was once used to be recovered from Le Blanc *alkali waste* containing calcium sulphide—Le Blanc process of soda ash manufacture being obsolete, the recovery process is no longer in use. Hydrogen sulphide, liberated by passing carbon dioxide through a suspension of alkali waste in water, is oxidised to sulphur by passing a mixture of the gas and air over heated iron oxide.

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S \; ;$$

$$2H_2S + O_2 = 2H_2O + 2S.$$

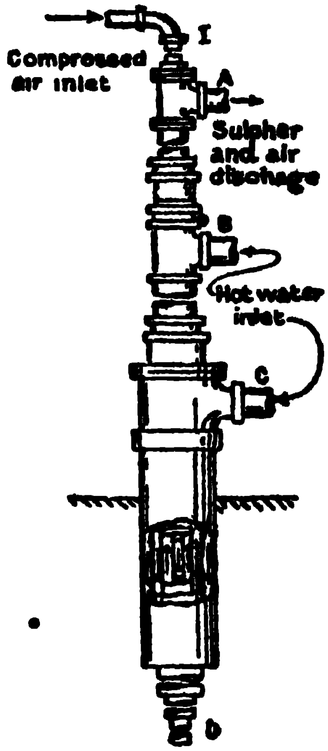


Fig. 116

Allotropy of sulphur.—Many allotropic forms of sulphur exist which differ markedly in their physical properties. The two common *crystalline* forms : (i) *rhombic* or α-sulphur, (ii) *monoclinic* or β-sulphur, and the three amorphous forms : (i) *plastic* or γ-sulphur, (ii) *milk of sulphur*, (iii) *colloidal sulphur.*

Rhombic sulphur.—It is best prepared by slowly evaporating a solution of roll sulphur in carbon disulphide—transparent lemon-yellow octahedral crystals (fig. 25) deposit, density 2.06 ; its m.p. is 112.8. *It is soluble in CS_2.* It is the most stable form at ordinary temperature—most other forms pass into it on keeping. Its formula is S_8.

Monoclinic sulphur.—It is *soluble in carbon disulphide*—the solution on evaporation yields α-sulphur. Its m.p. is 118.75° and density 1.96. Its formula is S_8. Unstable at ordinary temperature, it passes into rhombic form on standing.

It is experimentally found that above 95.5° monoclinic sulphur is stable, and below 95.5° rhombic sulphur is stable, while at 95.5° both the forms are stable and remain in equilibrium—this is the **transition temperature** for the two crystalline forms of sulphur : $S\alpha \rightleftharpoons S\beta$. The transformation is reversible.

Monoclinic or β-sulphur is prepared by allowing fused sulphur to cool slowly. A large porcelain crucible is nearly filled with pieces of roll sulphur, and *gently* heated on a sand bath until the whole of sulphur is just fused. It is then allowed to cool until a crust is formed on the surface. The crust is pierced at two points with a pointed glass rod, and the still liquid sulphur is poured out. On removing the surface crust, transparent yellow needle-shaped crystals of β-sulphur, also called **prismatic sulphur**, are found inside the crucible (fig. 26).

Liquid Sulphur.—Molten sulphur undergoes a series of changes when it is slowly heated to its boiling point. Sulphur melts at 112.8° into a clear *yellow mobile liquid* which *darkens* in colour as the temperature is raised and becomes *deep orange red*, but it remains mobile until the temperature reaches about 180° when the mobility is lost and the liquid suddently becomes very *viscous ;* on further heating the colour continues to darken ; the liquid is black and viscous at 230°, but the mobility is, however, gradually regained beyond 230°—the liquid becoming almost black at the boiling point, 444.6° ; on slowly cooling the boiling sulphur the same colour and viscosity changes occur in the reverse order.

The changes in viscosity are due to the fact that molten sulphur contains two allotropes $S\lambda$ (soluble in CS_2) and $S\mu$ (insoluble in CS_2) in equilibrium :

$S\lambda \rightleftharpoons S\mu$—the precentage of $S\mu$ at 120° is 3.6 but it increases with temperature. The action of heat on sulphur may be represented as :

$$\underset{\text{solid}}{S\alpha \xrightleftharpoons{96^\circ} S\beta} \xrightleftharpoons{120^\circ} \underset{\text{liquid}}{S\lambda \xrightleftharpoons{160^\circ} S\mu} \xrightleftharpoons{444.6^\circ} \underset{\text{vapour}}{S_8 \xrightleftharpoons{1000^\circ} S_2}$$

Plastic sulphur.—Small pieces of roll sulphur are heated in a large test tube until they melt to a clear mobile liquid. When this liquid sulphur, heated nearly to its boiling point, is poured in a thin stream in cold water, it solidifies to rubber-like elastic transparent yellow threads, called *plastic sulphur* or γ-sulphur, density 1.92.

It is insoluble in carbon disulphide, as it consists mostly of $S\mu$. It passes into rhombic form on standing. Plastic sulphur consists of chain of sulphur atoms and hence it can be stretched.

(*Liquid sulphur*) $S\lambda \rightleftharpoons S\mu \xrightarrow{\qquad\qquad}$ plastic sulphur.

Milk of Sulphur.—This a variety of white amorphous sulphur. Powdered roll sulphur when boiled with milk of lime dissolves, forming calcium pentasulphide and thiosulphate ; the orange-yellow liquid is filtered and acidified with dilute hydrochloric acid when milk of sulphur is deposited.

$$12S + 3Ca(OH)_2 = 2CaS_5 + CaS_2O_3 + 3H_2O.$$

$$2CaS_5 + CaS_2O_3 + 6HCl = 3CaCl_2 + 12S + 3H_2O.$$

Milk of sulphur is soluble in carbon disulphide, and is used in medicine. It passes into rhombic sulphur on heating. It is a form of $S\lambda$.

Colloidal Sulphur.—A turbid and milky colloidal suspension of sulphur is prepared by acidifying a solution of sodium thiosulphate or by passing hydrogen sulphide into a solution of sulphur dioxide :

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2 + S$$

$$2H_2S + SO_2 = 2H_2O + 3S.$$

The addition of a little alum coagulates colloidal sulphur. Some forms of colloidal sulphur are *soluble in carbon disulphide*, and others insoluble. It is used medicinally.

Uses of Sulphur.—(i) Huge quantities of sulphur are burnt to sulphur dioxide, which is either converted to sulphuric acid or to calcium bisulphite which is used in paper-making.

(ii) Sulphur is also used for making carbon disulphide, sulphur chloride, sodium thiosulphate, ultramarine, gunpowder, matches, dyes, and in vulcanising rubber and in fire works.

(iii) It finds use in medicine, and as a *fungicide in agriculture* in vineyards.

Properties of sulphur.—(i) Sulphur is a pale yellow brittle solid, non-conductor of heat and electricity, and boils at 444.6° giving deep red vapours—the temperature is definite to be used as a fixed point in thermometry. Sulphur vapour contains mainly S_8 and S_2 molecules in equilibrium : $S_8 \rightleftharpoons 4S_2$. Rhombic sulphur melts at 112.8°, and monoclinic sulphur at 118.75°. Sulphur is insoluble in water. Crystalline sulphur dissolves in carbon disulphide (from which it is often recrystallised), and in hot benzene and turpentine—plastic sulphur is insoluble in carbon disulphide.

(ii) It burns with a pale blue flame in air or oxygen, forming sulphur dioxide mainly and a little sulphur trioxide.

(iii) It directly unites, under the influence of heat with hydrogen, halogens (except iodine), carbon phosphorus, and most metals, forming sulphides.

(a) Hydrogen sulphide is obtained by passing hydrogen and sulphur vapour over red-hot pumice stone : $H_2 + S = H_2S$.

(b) A thin strip of copper catches fire in sulphur vapour, yielding copper sulphide : $Cu + S = CuS$.

(c) Sulphur burns spontaneously in fluorine, forming sulphur hexafluoride which is a stable gas, insoluble in water : $S + 3F_2 = SF_6$.

(d) Sulphur monochloride, an orange yellow liquid, is made by passing chlorine into boiling sulphur : $2S + Cl_2 = S_2Cl_2$. It dissolves sulphur.

(iv) Hot concentrated sulphuric and nitric acids oxidise sulphur to sulphur dioxide and sulphuric acid respectively.

$$S+2H_2SO_4 = 3SO_2+2H_2O \text{ ; } S+6HNO_3 = H_2SO_4+6NO_2+2H_2O.$$

(v) Sulphur dissolves in hot alkali giving sulphide and thiosulphate ; the sulphide combines with more sulphur, forming poly-sulphide, such as K_2S_2.

$$4S+6KOH = 2K_2S + K_2S_2O_3 \text{ (potassium thiosulphate) } + 3H_2O.$$

A brown mass called *liver of sulphur* is made by fusing a mixture of sulphur and potassium carbonate :

$$6S + 3K_2CO_3 = 2K_2S_2 + K_2S_2O_3 + 3CO_2.$$

Identity of Allotropes of Sulphur.—The identity of different allotropes of sulphur may be established by burning equal weights of the different forms in oxygen, when equal weights of the same product, viz., sulphur dioxide, are obtained :

$$S + O_2 = SO_2.$$

About 0.5 gm. of sulphur is accurately weighed out in a porcelain boat which is then introduced into the hard glass tube C (fig. 124). The sulphur is gently heated in a current of *dry* oxygen (which is bubbled through strong sulphuric acid in A for drying). The sulphur dioxide formed is absorbed in the previously weighed soda lime tubes B. The increase in weight gives the weight of sulphur dioxide produced.

The method of combustion of sulphur in oxygen is less accurate : a still better method is to oxidise equal weights of different forms of sulphur to sulphuric acid by heating with fuming nitric acid and precipitate the sulphuric acid formed as barium sulphate by means of barium chloride solution ; the precipitate is filtered, washed, dried and weighed. Equal weights of barium sulphate are obtained. 1 gm. of sulphur yields 7.28 gms. of $BaSO_4$.

Hydrides of Sulphur.—Two important hydrides of sulphur are :

Hydrogen sulphide, H_2S, a colourless gas, b. p. −60.7° and m. p. −85.6° ; critical temperature 100.40° and critical pressure 89.05 atm. Solubility in 1 vol. water 4.37 vols. at 0°, 2.6 vols. 20°.

Hydrogen persulphide, H_2S_2, a pale yellow oily liquid, readily decomposed by water and alkalis.

Hydrogen Sulphide or Sulphuretted hydrogen, H_2S.

Occurrence.—Hydrogen sulphide is found in volcanic gases and in many spring waters. As a product of putrefaction of sulphur-containing material, it is present in sewer gas. The unpleasant smell of putrefied hides and rotten eggs is partly due to this gas. The atmosphere usually contains a trace of it, which causes silver objects to tarnish owing to the formation of a film of black silver sulphide.

Laboratory preparation.—Hydrogen sulphide is usually prepared in the laboratory by the action of cold dilute sulphuric acid (1 vol. acid and 6 vols. water) upon pieces of ferrous sulphide taken in a Woulf's bottle fitted with a thistle funnel and a delivery tube—the gas is collected *by the upward displacement of air.* The gas may be washed with a little water and collected over hot water, if it is not required dry. It may be dried with fused calcium chloride or phosphorus pentoxide, (but *not with concentrated sulphuric acid which is reduced to sulphur dioxide* : $H_2SO_4+H_2S = 2H_2O+SO_2+S$) and then collected in dry jars by the displacement of air.

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

Ferrous sulphate is obtained as a by-product. Kipp's apparatus is used to obtain a ready supply of the gas for use in the laboratory.

Unless dry and free from oxygen, the hydrogen sulphide attacks mercury and tarnishes it.

Purification.—(i) Besides acid spray, the gas so prepared always contains some hydrogen evolved by the action of the acid upon free iron, invariably present in ferrous sulphide which is made by fusing iron and sulphur together. The gas is freed from acid spray by passing through a saturated solution of sodium hydrogen sulphide, $NaHS + HCl = NaCl + H_2S$, and from moisture by phosphorus pentoxide, and then cooled with solid carbon dioxide, when hydrogen sulphide liquefies and hydrogen passes out.

(ii) The impure gas is passed into a suspension of magnesium oxide in water, when only hydrogen sulphide is absorbed forming magnesium hydro sulphide which evolves pure H_2S on heating to 60°C.

$$MgO + 2H_2S \rightleftharpoons Mg(HS)_2 + H_2O.$$

Pure hydrogen sulphide free from hydrogen is prepared by the action of hot concentrated hydrochloric acid upon antimony sulphide. The gas is washed with water to remove hydrochloric acid, and dried over phosphorus pentoxide.

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

The purest hydrogen sulphide is best obtained by passing hydrogen and sulphur vapour over finely divided nickel at 450° : $H_2 + S \rightleftharpoons H_2S$.

Properties.—(i) A colourless, heavier-than-air gas, with the smell of rotten eggs, hydrogen sulphide is very poisonous in concentration above 0.1 per cent ;

It may prove fatal if inhaled for long—the antidote is *very much dilute chlorine.*

(ii) It does not support combustion, but it burns with a blue flame in excess of air or oxygen, giving water and sulphur dioxide ; but sulphur is deposited, if the supply of oxygen is limited—hence the *presence of sulphur* in the gas. The gas is also oxidised to sulphur, when mixed with air and passed over heated iron oxide :

$$2H_2S + 3O_2 = 2H_2O + 2SO_2 \; ; \; 2H_2S + O_2 = 2H_2O + 2S.$$

(iii) It is fairly soluble in cold water—the solution is a *weak dibasic acid* which reacts with alkali, giving sulphide and hydrosulphide :

$H_2S+2NaOH = Na_2S+2H_2O$; $H_2S+NaOH = NaHS+H_2O$

Left in contact with air, the solution of hydrogen sulphide becomes turbid due to the separation of sulphur by atmospheric oxidation.

$$2H_2S + O_2 = 2H_2O + 2S.$$

(iv) *Hydrogen sulphide is a reducing agent :*

(a) When hydrogen sulphide is passed into chlorine or bromine water, or into iodine suspended in water, sulphur is deposited and the halogens are reduced to their hydracids :

$$Cl_2 + H_2S = 2HCl + S \; ; \quad I_2 + H_2S = 2HI + S.$$

(b) Hydrogen sulphide reduces sulphur dioxide in presence of moisture : $SO_2 + 2H_2S = 2H_2O + 3S.$

(c) Hydrogen sulphide reduces ferric salts to ferrous salts ; thus it reduces yellow ferric chloride solution into colourless ferrous chloride, sulphur being deposited : $2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$

(d) It reduces *pink* solution of potassium permanganate acidified with dilute sulphuric acid to a colourless solution, with deposition of sulphur. It also reduces potassium dichromate solution acidified with dilute sulphuric acid—the orange-red colour of the solution turning green, with precipitation of sulphur :

$$2KMnO_4 + 3H_2SO_4 + 5H_2S = K_2SO_4 + 2MnSO_4 + 8H_2O + 5S.$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

(e) Sulphur is deposited when hydrogen sulphide is passed into concentrated sulphuric acid, and *hence the latter is not used in drying the gas.* It also reduces nitric acid, sulphur being deposited, and hence *the acid is not used in the preparation of the gas :*

$$H_2SO_4+H_2S = 2H_2O+SO_2+S \; ; \; 2HNO_3+H_2S = 2H_2O+2NO_2+S$$

(v) The gas is decomposed into its elements under the influence of electric sparks or when passed through a red-hot tube.

Metallic sulphides.—Hydrogen sulphide is used **as a reagent in qualitative analysis.** The gas precipitates sulphides of many metals with characteristic colours from solutions of their salts. Many sulphides are precipitated from solutions *acidified* with dilute hydrochloric acid—copper, lead, mercury and bismuth salts, all give *black* sulphide ; cadmium and arsenic give *yellow sulphide ;* antimony, an orange-yellow sulphide ; tin (stannous), a brown sulphide.

$$CuSO_4+H_2S = H_2SO_4+CuS \quad HgCl_2+H_2S = 2HCl+HgS$$

$$CdCl_2+H_2S = 2HCl+CdS \; ; \quad SnCl_2+H_2S = 2HCl+SnS.$$

Many sulphides are precipitated only in *alkaline solution ;* in ammoniacal solution zinc salts give a *white* sulphide ; manganese, a *flesh-coloured* sulphide ; iron, cobalt and nickel, all give *black* sulphide.

$$ZnSO_4 + (NH_4)_2S = ZnS + (NH_4)_2SO_4 \; ;$$

$$FeSO_4 + (NH_4)_2S = FeS + (NH_4)_2SO_4 \; ;$$

Sulphides of alkali metals are soluble in water ; sulphides of alkaline earth metals are sparingly soluble, but they react with water giving soluble hydrosulphides : $2CaS + 2H_2O = Ca(HS)_2 + Ca(OH)_2$, aluminium and chromium sulphides are decomposed by water forming the hydroxide :

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S.$$

Metallic Sulphides
- Soluble in water. Sulphides of alkali & alkaline earth metals.
- Insoluble in water
  - Solube in dil. HCl but insoluble in ammonium hydroxide—sulphides of Fe, Co, Ni, Zn and Mn.
  - Insoluble in dil. HCl—sulphides of Hg, Pb, Bi, Cu, Cd, As, Sn and antimony.

H_2S is generally used **as a reagent in qualitative analysis** for :

(i) **the identification of metals** from the distinctive colours of their sulphides ;

(ii) **the classification of metals** into groups according to the solubility of metallic sulphides in water, acid and alkali ; and

(iii) **the separation of metals** of different groups from a solution of the salts—thus when hydrogen sulphide is passed into a hot solution containing salts of *copper, zinc and sodium*, and acidified with dilute hydrochloric acid, only black copper sulphide precipitates which is separated by filtration. On passing H_2S into the filtrate, made alkaline with ammonia, white zinc sulphide precipitates, the sodium salt remains in solution.

Tests.—Hydrogen sulphide is recognised (i) by its smell of rotten eggs, (ii) in its staining silver coin black due to formation of a film of silver sulphide. (iii) by its turning lead acetate paper *black* due to the formation of lead sulphide, $Pb(CH_3COO)_2 + H_2S = PbS + 2CH_3COOH$, and (iv) by the production of *purple colour* with alkaline sodium nitroprusside solution—alkali sulphide solution (but not free hydrogen sulphide) responds to this test.

The presence of sulphide in insoluble sulphides is detected by reduction with nascent hydrogen (heating the sulphide with zinc and strong hydrochloric acid) when hydrogen sulphide evolves, which turns lead acetate paper black. Alternatively, the sulphide is fused with sodium carbonate and the mass extracted with water—the extract gives a purple colour with sodium nitroprusside solution.

Hydrogen sulphide may be prepared in the laboratory by heating an intimate mixture of sulphur, paraffin and shredded asbestos.

Absorbent.—An acidic gas H_2S is absorbed by the caustic alkalis, NaOH and KOH ; lead nitrate solution also absorbs the gas.

$$Pb(NO_3)_2 + H_2S = 2HNO_3 + PbS \text{ (black precipitate).}$$

Composition.—The formula of hydrogen sulphide is determined by heating tin or copper foil in the gas ; $H_2S + Sn = H_2 + SnS$.

A thumb-tube (fig. 97) is filled with mercury and inverted over mercury in a trough. A few c.c. of pure and dry hydrogen sulphide is introduced in the tube, and a *piece of tin* is placed in the horizontal portion of the tube. The bit of tin is heated, when it reacts with hydrogen sulphide, forming tin sulphide and *liberating hydrogen*. The apparatus is allowed to cool. The mercury is found to stand at the same level as before. Hence, the volume of hydrogen liberated is equal to the volume of hydrogen sulphide decomposed, *or hydrogen sulphide contains its own volume of hydrogen.*

1 c.c. of hydrogen sulphide contains 1 c.c. of hydrogen.

∴ 1 molecule of hydrogen sulphide contains 1 molecule of hydrogen. (Avogadro's hypothesis)

∴ its formula is H_2S_x. The vapour density of the gas is 17, and hence the mol. wt. 34.

∴ $2 \times 1 + 32x = 34$, or $x = 1$. The formula is H_2S.

When dry hydrogen sulphide is sparked in a graduated tube over mercury (fig. 95), it decomposes into hydrogen and solid sulphur without any change in volume, and hence contains its own volume of hydrogen.

Oxides and oxyacids of sulphur.—Two important oxides of sulphur with their corresponding oxyacids are :

Sulphur dioxide, SO_2	Sulphurous acid, H_2SO_3.
Sulphur trioxide, SO_3	Sulphuric acid, H_2SO_4.

Sulphur dioxide, SO_2 b.p. −10.0° ; m.p. −72.7° ; critical temperature 157.2°. Solubility in water, 45 vols. in 1 vol. H_2O at 15°C.

History, etc.—Homer (900 B.C.) mentions the use of burning sulphur in fumigation. Priestley (1774) obtained the gas by heating mercury with concentrated sulphuric acid. The gas is found in volcanic gas, and in some springs of volcanic districts, and also in the atmosphere of the manufacturing towns where it originates from the combustion of coal.

Laboratory Preparation.—The gas is prepared in the laboratory by reducing concentrated sulphuric acid with copper. Copper turnings are taken in a flask (Fig. 117) fitted with a thistle funnel and a delivery tube. Concentrated sulphuric acid is poured down the funnel to cover the copper, and the flask is then slowly heated till sulphur dioxide is evolved with effervescence. The gas is collected *by upward displacement of air.* It may be dried by concentrated sulphuric acid, calcium chloride or phosphorous pentoxide, and collected over mercury.

$$2H_2SO_4 + Cu = CuSO_4 + 2H_2O + SO_2.$$

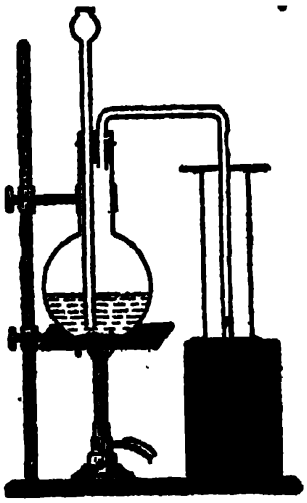


Fig. 117

Concentrated sulphuric acid may also be reduced to sulphur dioxide by heating with mercury, silver, sulphur or charcoal.

$$Hg+2H_2SO_4 = HgSO_4+2H_2O+SO_2 ; \; 2Ag+2H_2SO_4 = Ag_2SO_4+2H_2O+SO_2.$$
$$S+2H_2SO_4 = 3SO_2+2H_2O ; \; C+2H_2SO_4 = 2SO_2+2H_2O+CO_2.$$

The gas is readily obtained without heating by dropping concentrated sulphuric acid into a solution of sodium hydrogen sulphite :

$$NaHSO_3 + H_2SO_4 = NaHSO_4 + H_2O + SO_2.$$

Industrial preparation.—Sulphur dioxide is obtained industrially by burning sulphur in air. The gas is dissolved out from the products of combustion by a descending stream of cold water in a tower. The sulphur dioxide is boiled out of the resulting solution, dried by refrigeration and concentrated sulphuric acid, liquefied under pressure, and stored in steel cylinders.

It may also be obtained by roasting *sulphide minerals*, such as iron pyrites, copper pyrites, and zinc blende, or *spent iron oxide.*

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2\ ;\quad 2ZnS + 3O_2 = 2ZnO + 2SO_2.$$

The gas (mixed with CO_2 and nitrogen) is obtained now-a-days by heating gypsum with clay, sand and coke, and is used for making sulphuric acid.

Properties.—(i) A colourless, heavier-than-air gas with a chcking smell of burnt sulphur, sulphur dioxide is easily liquefied by pressure (2.5 atmosphere at 15°) or by cooling in a freezing mixture.

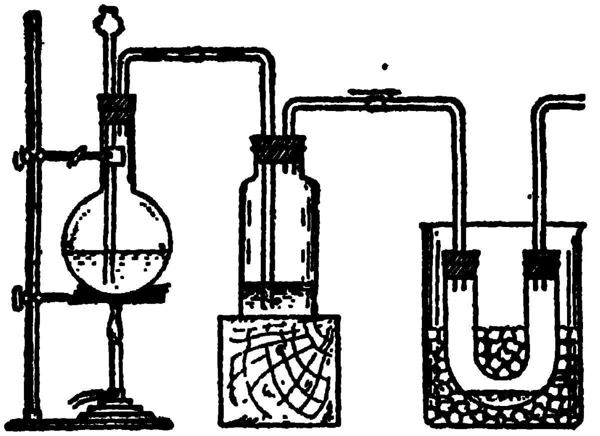


Fig. 118

The gas is dried by passing through concentrated sulphuric acid and then condensed to a colourless liquid in a tube (fig. 118) cooled in a freezing mixture. It is also liquefied by a pressure of 2.5 atmospheres at 15°. The liquid is a non-conductor of electric current but is a good solvent for substances, such as sulphur, phosphorus, iodine, resins and some salts like potassium iodide. The liquid is kept in iron cylinders and is used as a source for the gas, and for refining petroleum.

(ii) An incombustible gas, it does not support the combustion of hydrogen or a taper, but heated potassium, tin, iron, and magnesium burn in the gas. $4K + 3SO_2 = K_2SO_3 + K_2S_2O_3$ (potassium thiosulphate).

(iii) It is highly soluble in water—the solution smells strongly of the gas and is *acidic* due to the formation of unstable *sulphurous acid,* $H_2O + SO_2 \rightleftharpoons H_2SO_3$, known in solution only—the acid is dibasic and forms *acid sulphites,* also called *bisulphites,* such as $NaHSO_3$, and normal sulphites such as Na_2SO_3. The sulphur dioxide is expelled from its solution by boiling.

(iv) *An acidic oxide,* it is *absorbed* by alkalis to yield bisulphites and sulphites :

$$NaOH + SO_2 = NaHSO_3\ ;\quad NaHSO_3 + NaOH = Na_2SO_3 + H_2O.$$

(*a*) Crystals of normal sodium sulphite is obtained as follows :—A solution of sodium hydroxide is made into two equal parts—one portion is saturated with sulphur dioxide to yield sodium bisulphite solution. This is added to the remaining portion of sodium hydroxide solution, and the liquid evaporated, when crystals of sodium sulphite, Na_2SO_3, $7H_2O$ separate on cooling.

Sodium bisulphite solution is acid in reaction, while sodium sulphite solution is slightly alkaline due to hydrolysis :

$$HSO_3' \rightleftharpoons H^+ + SO_3''\ ;\quad Na_2SO_3 + H_2O \rightleftharpoons NaHSO_3 + NaOH.$$

Sodium bisulphite is known in solution only—the solution on evaporation in presence of excess sulphur dioxide yields sodium-metablisulphite, $Na_2S_2O_5$, used in photography. $2NaHSO_3 = Na_2S_2O_5 + H_2O$.

Sodium carbonate solution reacts similarly, yielding sodium bisulphite, which then reacts with more sodium carbonate to form sodium sulphite : $Na_2CO_3+H_2O+2SO_2 = 2NaHSO_3+CO_2$.

$$2NaHSO_3+Na_2CO_3 = 2Na_2SO_3+CO_2+H_2O.$$

(b) Sulphur dioxide turns lime water milky due to the formation of insoluble calcium sulphite, which dissolves (and hence the milkiness disappears) in excess of the gas, yielding calcium bi-sulphite : (cf. CO_2). Milk of lime reacts similarly, yielding calcium bi-sulphite.

$$Ca(OH)_2+SO_2=CaSO_3+H_2O \;;\quad CaSO_3+H_2O+SO_2=Ca(HSO_3)_2.$$

Both CO_2 and SO_2 turn lime water milky. Hence to detect carbonate in presence of sulphite, the solid mixture is treated with dilute sulphuric acid and the evolved gases passed into a tube containing an acidified (with dilute sulphuric acid) solution of potassium dichromate which turns green and the SO_2 is removed at the same time —the residual gas which is CO_2, turns lime water milky.

(v) *It is a reducing agent.*—A solution of sulphur dioxide or sulphite slowly absorbs oxygen from the air to form sulphuric acid, the reaction is catalysed by trace of copper or iron salts. Chlorine, bromine or iodine oxidise it immediately to sulphuric acid.

$$2H_2SO_3+O_2 = 2H_2SO_4 \;;\quad Cl_2+SO_2+2H_2O = H_2SO_4+2HCl.$$

It *decolorises* an acidified solution of potassium permanganate by reduction. It reduces an acidified solution of potassium dichromate, the colour of the solution changing from *orange-yellow to green.*

$$2KMnO_4+5SO_2+2H_2O = K_2SO_4+2MnSO_4+2H_2SO_4.$$

$$K_2Cr_2O_7+3SO_2+H_2SO_4 = K_2SO_4+Cr_2(SO_4)_3+H_2O.$$

Sulphur dioxide is readily oxidised by hydrogen peroxide :

$$H_2O_2 + H_2SO_3 = H_2O + H_2SO_4.$$

Sulphur dioxide liberates iodine from an iodate, but the iodine is decolorised with excess of sulphur dioxide :

$$2KIO_3 + 5SO_2 + 4H_2O = I_2 + 3H_2SO_4 + 2KHSO_4.$$

$$I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4.$$

It reduces ferric salts to ferrous salts :

$$2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + 2HCl + H_2SO_4.$$

(vi) *Oxidising action of sulphur dioxide.*—It oxidises moist hydrogen sulphide to sulphur : $2H_2S + SO_2 = 2H_2O + 3S$.

Sulphur dioxide oxidises white-hot coke to carbon dioxide—the reaction is used to recover sulphur from waste gases containing sulphur dioxide. In strongly acid solution sulphur dioxide oxidises ferrous chloride :

$$SO_2 + C = CO_2 + S \;;\quad 4FeCl_2 + 4HCl + SO_2 = 4FeCl_3 + 2H_2O + S.$$

(vii) Sulphur dioxide possesses *bleaching properties in presence* of moisture. *Moist* coloured flowers are bleached colourless by sulphur dioxide, but not the *dry flowers.* Magenta solution is decolorised by the gas, but not litmus. The bleaching is due to the reduction of the colours to colourless compounds by nascent hydrogen, thus :

$$\text{Colouring matter} + H_2O + H_2SO_3 = \text{Colourless reduction product} + H_2SO_4.$$

Bleaching properties of sulphur dioxide and chlorine.—(a) *Sulphur dioxide by reduction* (cf. *chlorine which bleaches in presence of moisture by oxidation*).

(b) *Sulphur dioxide is a milder bleaching agent than chlorine*, and hence delicate fabrics, such as wool, silk, straw for hats, etc., which are likely to be injured by chlorine, are bleached by sulphur dioxide.

(c) The original colour of fabrics bleached by sulphur dioxide may sometimes be *restored*, on exposure to air, by the oxidising action of air and light, but *the bleaching action of chlorine is always permanent.*

(viii) When heated to 150° in a sealed tube, a solution of sulphuorus acid deposits sulphur, **showing the presence of sulphur in sulphur dioxide :** $2H_2SO_3 + SO_2 = 2H_2SO_4 + S$.

(ix) Sulphur dioxide reacts with heated lead dioxide and sodium peroxide, yielding metallic sulphate :

$$PbO_2 + SO_2 = PbSO_4 \; ; \quad Na_2O_2 + SO_2 = Na_2SO_4.$$

(x) Sulphur dioxide reacts with oxygen in the presence of heated platinum, yielding sulphur-trioxide, and with chlorine in bright sunlight or in presence of charcoal, giving sulphuryl chloride.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \; ; \quad SO_2 + Cl_2 = SO_2Cl_2.$$

Composition.—The composition is determined both volumetrically and gravimetrically, exactly in the same way as for carbon dioxide—only sulphur is being burnt in oxygen instead of charcoal.

Tests.—(i) The gas is detected by its smell of burnt sulphur. (ii) A piece of paper soaked in acidified solution of potassium dichromate is turned green by sulphur dioxide. (iii) Any sulphite or bisulphite, on treatment with dilute hydrochloric or sulphuric acids, liberates sulphur dioxide, which may be recognised as above.

(iv) With barium chloride solution a sulphite solution gives a white precipitate of barium sulphite, soluble in hydrochloric acid ($BaSO_4$ is insoluble)—oxidising agents such as chlorine or bromine water precipitates barium sulphate from the solution :

$$BaSO_3 + H_2O + Br_2 = BaSO_4 + 2HBr.$$

Uses.—(i) In the manufacture of sulphuric acid, in the refining of sugar and kerosene oil, and for bleaching delicate materials such as wool, silk and straw ; (ii) In the preparation of sodium and calcium bisulphites, both used for paper-making, and sodium metabisulphite, used in photography ; (iii) Sulphur dioxide has antiseptic properties and is used in fumigation and in preserving fruits ; (iv) Liquid sulphur dioxide is a refriggrant ; (v) The gas is also used as an *antichlor* in removing excess chlorine from bleached materials.

Absorbent.—An acidic oxide, SO_2 is absorbed by the alkalis, NaOH and KOH.

Thionyl chloride, $SOCl_2$, is made by passing sulphur dioxide over phosphorus penta chloride :

$$SO_2 + PCl_5 = SOCl_2 + POCl_3$$

This is a colourless liquid, b. pt. 78°, and is separated from phosphorous oxychloride b. pt. 107° by fractional distillation. It fumes in moist air and is readily hydrolysed by water, forming sulphurous and hydrochloric acids :

$$SOCl_2 + 2HOH = H_2SO_3 + 2HCl.$$

Sulphur trioxide, SO_3

Sulphur trioxide, or sulphuric anhydride, SO_3, is prepared by passing a mixture of sulphur dioxide and air or oxygen over platinised asbestos heated to 450° in a glass tube and collecting the trioxide in a receiver cooled in freezing mixture:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3.$$

It may also be obtained by heating ferric sulphate or pyro-sulphuric acid, $H_2S_2O_7$, or by distilling concentrated sulphuric acid over phosphoruous pentoxide:

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3 \; : \; H_2S_2O_7 = H_2SO_4 + SO_3$$
$$H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3.$$

Sulphur trioxide exists in two forms: α-sulphur trioxide, colourless needles, m.p. 17°, and β-sulphur trioxide, an asbestos-like solid, which sublimes at 50°. The α-form transforms into the β-form on keeping in presence of moisture.

It fumes in moist air, and reacts violently with water, forming sulphuric acid, and pyrosulphuric acid, also called **oleum.**

$SO_3 + H_2O = H_2SO_4$; $2SO_3 + H_2O = H_2S_2O_7$ (oleum). It directly unites with basic oxides, forming sulphates. $Na_2O + SO_3 = Na_2SO_4$; $BaO + SO_3 = BaSO_4$.

Sulphuric Acid, Oil of Vitriol, H_2SO_4

History.—The acid was obtained by the mediaeval alchemists who called it *oil of vitriol*, by distilling green vitriol and absorbing the vapours in water.

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3 \; ; \; SO_3 + H_2O = H_2SO_4.$$

The acid was used to be made in the 18th century by burning sulphur and nitre in a deflagrating spoon under a glass bell-jar standing over water. The lead chamber process has been developed empirically out of this 18th century practice. The chamber process is being gradually displaced nowadays by the comparatively young contact process which developed late in the 19th century, mainly due to the efforts of German technologists. The importance of sulphuric acid in the industrial life of a country is unequalled by that of any other chemical commodity.

Manufacture.—Sulphuric acid is manufactured from sulphur dioxide by: (i) the lead chamber process, and (ii) the contact process.

The lead chamber process.—The principle of the chamber process is the oxidation of moist sulphur dioxide by the oxygen of air in presence of oxides of nitrogen which act as a catalyst. An intermediate compound nitroso-sulphuric acid, HO.SO$_2$.ONO, is formed by the interaction of sulphur dioxide, oxygen, oxides of nitrogen and water; the nitroso-sulphuric acid is readily decomposed by water into sulphuric acid and oxides of nitrogen, which react again:

$$2SO_2 + N_2O_3 + O_2 + H_2O = 2HO.SO_2.O.NO.$$
$$2HO.SO_2ONO + H_2O = 2HO.SO_2.OH + N_2O_3.$$

An alternative mechanism suggests that nitrogen dioxide oxidises sulphur dioxide to sulphur trioxide which with water yields sulphuric acid—the resulting nitric oxide is reoxidised by atmospheric oxygen to nitrogen dioxide, which reacts again:

$$SO_2 + NO_2 + H_2O = H_2SO_4 + NO \; ; \; 2NO + O_2 = 2NO_2.$$

The process is worked as follows. Sulphur dioxide is made by roasting iron pyrites, FeS_2, zinc blende, ZnS or elementary sulphur in a current of air in **burners** B.

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2 \; ; \; 2ZnS + 3O_2 = 2ZnO + 2SO_2$$

The burner gases (fig. 119) containing about 8 per cent sulphur dioxide, 10 per cent oxygen and the rest nitrogen, pass through a **nitre-oven** N, where oxides of nitrogen are supplied by distilling a mixture of sodium nitrate and strong sulphuric acid from *nitre pots* and then through a **dust-catcher,** K, containing baffle-walls, where the suspended dust deposits.

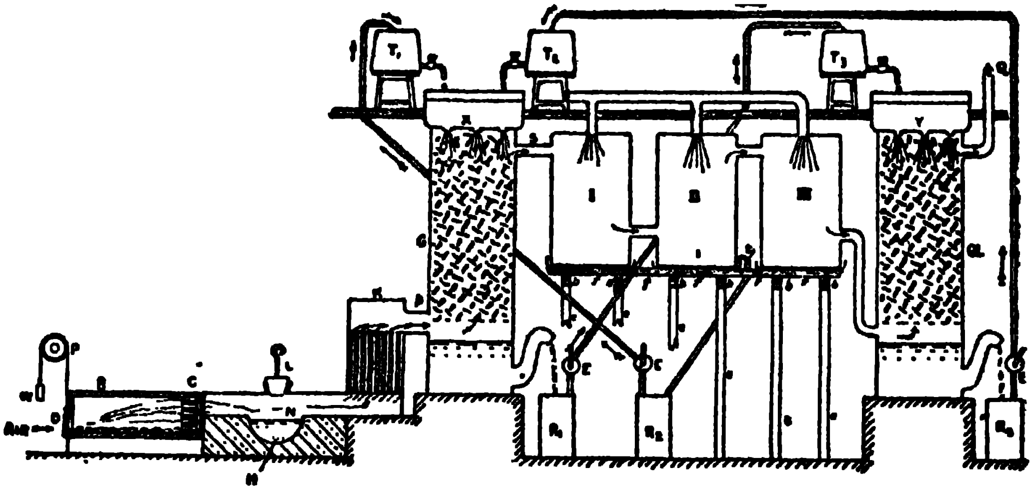


Fig. 119

In modern plants oxides of nitrogen are supplied by catalytic oxidation of ammonia.

From the dust-catcher the hot gases at about 300°-400° pass into the **Glover tower,** G—a lead tower lined with acid-resisting bricks and packed with flints down which are sprayed two streams of acid; (i) the dilute chamber acid and (ii) the nitroso-sulphuric acid formed in the Gay-Lussac tower.

The Glover tower serves (i) to cool the burner gases to about 50° to 60° before entering the chambers, (ii) to concentrate the dilute chamber acid (65—70% acid) to about 78 per cent H_2SO_4 for sale or for use in the Gay-Lussac tower, (iii) to decompose the acid from the Gay-Lussac tower by the water in the dilute chamber acid so as to release the oxides of nitrogen which are returned to the chamber with the burner gases.

$$2HO.SO_2.O.NO + H_2O = 2HO.SO_2.OH + N_2O_3.$$

Besides, about 25 per cent of the total yield of the acid is formed in the tower. Hence the modern trend is to replace the chambers by a number of towers, called *reaction towers.*

The 78 per cent concentrated acid is collected at the base of the Glover tower.

From the Glover tower the gases enter, by a lead main, a set of **lead chambers,** I, II, and III made of sheet lead welded together by oxy-hydrogen flame. Water is sprayed from the top of the chambers and dilute (65 to 70 per cent) sulphuric acid, formed by the interaction of sulphur dioxide, oxygen, oxides of nitrogen and water, collects on the floor of the chambers whence it is withdrawn and pumped to the top of the Glover tower for concentration. The strength of the chamber acid is kept at 65 to 70 per cent H_2SO_4 by regulated supply of water—still stronger acid attacks lead and also absorbs oxides of nitrogen, yielding nitroso-sulphuric acid, called **chamber crystals.** The chamber crystal may however be decomposed by admitting water in the chambers.

The gases from the last chamber, containing the valuable oxides of nitrogen, are led in the **Gay-Lussac tower,** Gl, a lead lined tower, packed with coke, down which flows a stream of 78 per cent sulphuric acid (from the base of the Glover tower) which absorbs the oxides of nitrogen as nitroso-sulphuric acid. The acid collected from the base of the Gay-Lussac tower is pumped to the top of the Glover tower for denitration—the oxides of nitrogen are returned to the chambers, and the cycle of reactions is repeated. The waste gas from the Gay-Lussac tower passes to a chimney which maintains a draught through the plant.

Concentration of chamber acid.—Chamber acid contains about 65 to 70 per cent sulphuric acid. It is usually concentrated to 78% H_2SO_4 by passing through Glover tower. It may also be concentrated by evaporation in lead pans to 78% H_2SO_4 after which lead rapidly dissolves in the hot acid. The 78 per cent acid is known as **brown oil of vitriol** or **B.O.V.** Stronger acid, 95% H_2SO_4 is made by concentrating the B.O.V. in a current of hot air swept over its surface.

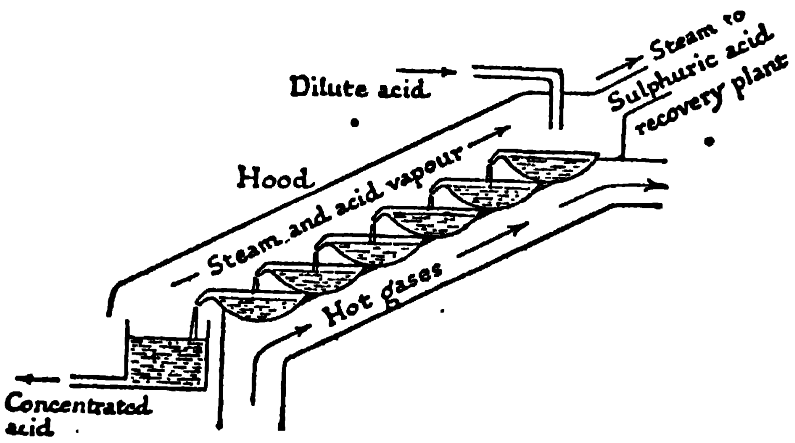


Fig. 120

In the cascade process (fig. 120) the acid is allowed to flow down a series of basins, made of silica or ferrosilicon such as *duriron* and *tantiron,* arranged one below the other, with the lip of one discharging into the basin next lower. The basins, resting on a staircase of acid-resisting bricks, are heated by a coke fire, and hot air sweeps over the surface of the acid. The concentrated acid, 96 per cent, is obtained from the last basin. It may be concentrated up to 98 per cent sulphuric acid by heating in in cast iron pans by direct fire. The strongest acid does not dissolve cast iron but the 95% acid does, and hence the latter is mixed with a bulk of 98% acid during concentration. The 98% acid may be brought to any desired strength by adding oleum ; i.e., sulphuric acid containing free sulphur trioxide. *The sulphuric acid is generally stored in stoneware bottles.*

Purification of chamber acid.—Commercial sulphuric acid contains lead sulphate, arsenious oxide (derived from arsenic in pyrites) and oxides of nitrogen as impurities. The metals are removed by diluting the acid to 60 per cent (when lead sulphate, insoluble in dilute acid, separates) and treating with hydrogen sulphide in lead tower—the insoluble sulphides of lead and arsenic are filtered off. The acid is then distilled with a little ammonium sulphate which decomposes oxides of nitrogen :

$$(NH_4)_2SO_4 + N_2O_3 = 2N_2 + H_2SO_4 + 3H_2O.$$

Water, nitrogen, etc. distil in the beginning—the distillate towards the end is 98% H_2SO_4 which may be made up to 100% by adding oleum.

Laboratory illustration of chamber process.—A large dry flask A (fig. 121) is fitted with a cork through which pass four long inlet tubes, almost reaching the bottom, and a short outlet tube which acts as an exit. The flask is connected with three Woulfe's bottles containing concentrated sulphuric acid, through which SO_2, NO and O_2 can be passed, and the flask B containing hot water. The four inlet tubes are meant for carrying inside the flask : (a) sulphur dioxide produced by heating copper turnings with concentrated sulphuric acid, (b) nitric oxide obtained by the action of dilute nitric acid upon copper turnings, (c) oxygen or air from hand bellows and (d) steam. As a result of interaction among sulphur dioxide, nitric oxide, air and steam sulphuric acid is formed, which collects in the flask.

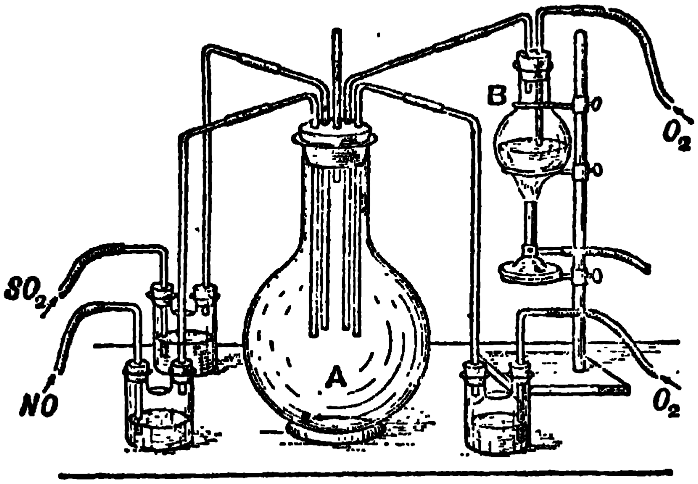


Fig. 121

At first a stream of oxygen is passed into A, and then NO (which forms red fumes with the oxygen) and next SO_2 are admitted, and finally water vapour by bubbling oxygen through hot water in B. White colourless crystals of nitrososulphuric acid deposit on the walls of A. On admitting steam the crystals dissolve forming sulphuric acid and red oxide of nitrogen.

$$2SO_2 + NO + NO_2 + O_2 + H_2O = 2HO.SO_2.O.NO$$
$$2HO.SO_2.O.NO + H_2O = 2HO.SO_2.OH + N_2O_3.$$

The contact process.—The process consists in bringing about the combination of sulphur dioxide and oxygen (in the form of air) to form sulphur trioxide by contact with a catalyst and the subsequent conversion of the sulphur trioxide into sulphuric acid.

(i) The formation of sulphur trioxide, as shown by the equation :

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45{,}000 \text{ calories},$$

is an *exothermic* reversible reaction, and is therefore favoured at low temperature. But at low temperature the rate of formation of sulphur trioxide is too slow. Hence the reaction is carried out

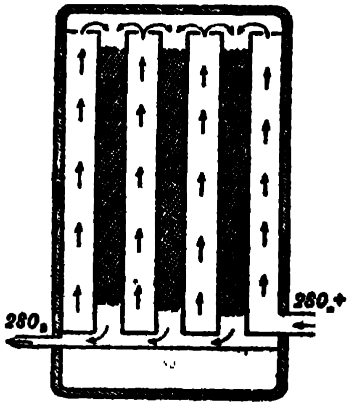


Fig. 122

at an **optimum temperature** of 450°C such that the speed of the reaction is not too slow, nor the yield of sulphur trioxide too low.

The decomposition of trioxide becomes increasingly greater as the temperature rises. For a burner gas composition, 7 p.c. SO_2, 10 p.c. O_2 and 83 p.c. N_2 by volume, the percentages of SO_2 oxidised to SO_3 at different temperature are: 434° 99; 550° 85; 740° 60.

(ii) A catalyst such as *platinised asbestos*, *vanadium pentoxide*, *platinised silica gel*, is used to hasten the attainment of the equilibrium state at the comparatively low optimum temperature.

Platinised asbestos is prepared by gently heating asbestos soaked in ammonium platini-chloride. The platinum salt decomposes and deposits a residue of finely divided platinum.

$(NH_4)_2PtCl_6 = 2NH_3 + 2HCl + 2Cl_2 + Pt.$

(iii) Excess of oxygen ensures complete conversion of sulphur dioxide to sulphur trioxide.

(iv) The catalyst loses its activity due to '*poisoning*' by arsenious oxide, sulphuric acid mist, and dust, etc., which are present in the burner gases, and hence the necessity of removing these impurities from sulphur dioxide before it enters the contact chamber.

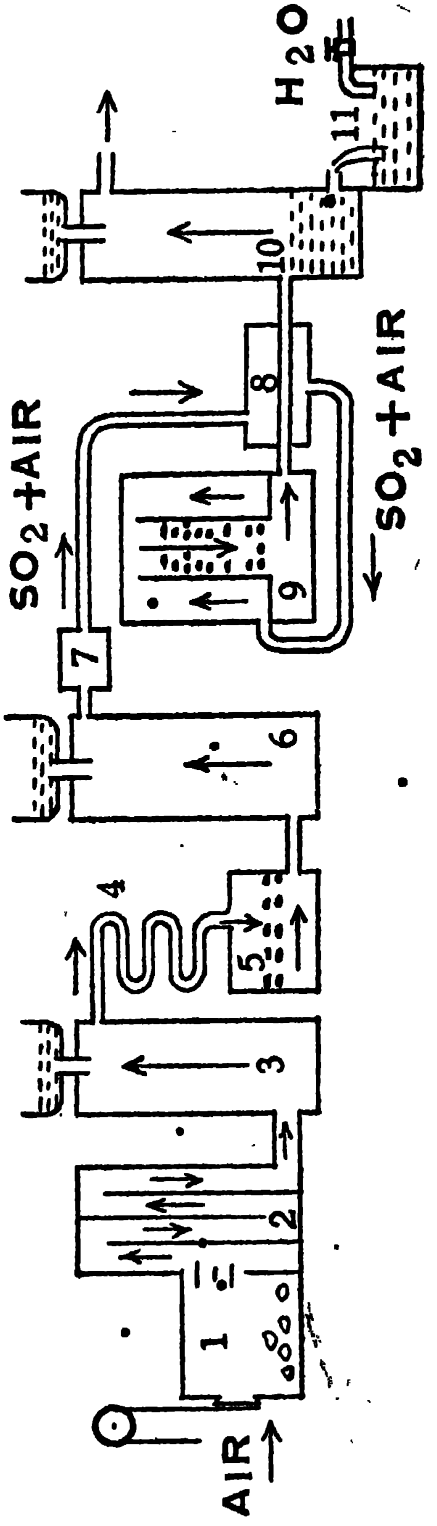


Fig. 23

Sulphur dioxide is produced by roasting iron pyrites or sulphur in a current of air in burners 1 (fig. 123). The gases from *pyrites burner* (1) containing about 8% sulphur dioxide, 10% oxygen and the rest nitrogen, are carefully purified by passing in succession through:

(i) a *dust chamber* 2, where the gas is cleared of its dust and iron oxide cloud, (ii) a *lead tower* 3, meeting a flow of concentrated sulphuric acid, which removes the arsenious oxide and also cools the gas somewhat, (iii) water-cooled *lead coils* 4 where the gas is cooled to room temperature, (iv) *coke filters* 5 to remove chlorine (present as HCl) and to arrest acid mist, (v) a *drying tower* 6 packed with coke down which 93 p.c. sulphuric acid is flowing. The *purified and dry* gas must be *optically* *clear,* i.e., no fog is visible when a beam of light is sent through it in a chamber 7. The gases are finally fed, via a *heat-interchanger* 8 where they are preheated by the hot sulphur trioxide and nitrogen leaving the converter, into an iron cylinder, called a converter 9, (also fig. 122) fitted inside with vertical iron tubes packed with *platinised asbestos.* The incoming gases circulate round the hot tubes and then pass down them when sulphur dioxide is converted into sulphur trioxide. *The catalyst is kept at the optimum temperature of* 450°. Since the reaction is exothermic, no external heating is needed after once the reaction has been started.

The sulphur trioxide leaving the converter, is *absorbed in* 98 *per cent sulphuric acid* in the tower 10. $SO_3 + H_2O = H_2SO_4$. Absorption of sulphur trioxide in water alone results in the formation of mist of droplets of acid. The strength of the absorption acid is kept at 98 per cent by regulated supply of water or dilute sulphuric acid.

If no water is added, sulphur trioxide dissolves in sulphuric acid, yielding **fuming sulphuric acid** or **oleum,** i.e., sulphuric acid containing dissolved SO_3.

Commercial strength of oleums are 15, 20, 30, 45, 60 and 65 per cent free SO_3. *Sulfan* is 100 p.c. oleum.

Comparison of chamber and contact acids.—(*i*) The chamber acid contains about 65 to 70 per cent of sulphuric acid; still stronger acid is obtained by special methods of concentration. The contact process directly produces 100 per cent sulphuric acid and oleum. (*ii*) The chamber acid is *impure* and contains arsenic, source being iron pyrites. The contact acid, on the other hand, is pure since the use of catalyst necessitates the purification of burner gases, and is particularly free from arsenic, and hence suitable for use in the preparation of edible products and for filling accumulators. (*iii*) The weak chamber acid is suitable for use in the manufacture of salt-cake, super-phosphate, ammonium sulphate and alum; the concentrated contact acid is used in the refining of petroleum, in synthetic dye and drug industries and in explosives.

The choice of the process, therefore, largely depends on the use of the acid. The contact process is rapidly displacing the chamber process.

The advantages of the platinum catalyst are: (i) 90 p.c. of the metal may be recovered, (ii) operating cost is less, as there is heavy royalty charge for vanadium catalyst, and (iii) initial capital cost of the plant is less, as it handles higher sulphur dioxide (8 to 10 p.c.) content gas. But its greatest drawback is that it readily gets *poisoned* and its activity declines with use—the life of the catalyst is consequently shorter.

Vanadium catalyst is immune to poisoning and hence retains its activity for a longer period than platinum. It gives little trouble during operation; its initial cost is also less. But the vanaduium mass handles a lower sulphur dioxide (7 to 8 p.c.) content gas, and it has no salvage value when once worn out. The platinum contact mass is being rapidly displaced by vanadium catalyst. Vanadium pentoxide contact plant works in several places in India, e.g., Tata Iron and Steel Works at Jamshedpur, Burma Oil Company at Digboi, and Bengal Chemical and Pharmaceutical Works at Calcutta.

Sometimes sulphur dioxide (mixed with CO_2) for making H_2SO_4 by contact process is obtained by heating a mixture of gypsum, coke, sand and clay in a rotary kiln, the residue being cement clinker of calcium silicate and aluminate.

$$2CaSO_4 + C + (xSiO_2 + yAl_2O_3) = 2SO_2 + CO_2 + (2CaO, xSiO_2, yAl_2O_3).$$

Properties of sulphuric acid.—(i) Pure sulphuric acid is a heavy (density 1.838 at 15°), colourless, oily liquid which freezes at

10.4°. It decomposes at its boiling point, yielding dense white fumes of sulphur trioxide, $H_2SO_4 \rightleftharpoons SO_3 + H_2O$ and forming a constant boiling mixture of 98.33 per cent sulphuric acid and water, boiling at 338°. 98 p.c. acid has a sp. gr. of 1.84.

(ii) Pure acid is a very poor electrical conductor but in aqueous solution it is a good conductor of heat and electricity.

(iii) It decomposes into sulphur dioxide, oxygen and water vapour when dropped on heated pumice stone (p. 179).

$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2.$$

The mixed gases are passed through : (i) a U-tube (kept in cold water) in which liquid drops condense—the liquid is recognised to be water by the blue colour it gives with anhydrous copper sulphate and hence the presence of hydrogen in sulphuric acid, and then a (ii) second U-tube (cooled in freezing mixture) in which sulphur dioxide condenses to a liquid and oxygen passes out. Sulphur separates when an aqueous solution of the sulphur dioxide is heated to 150° in a sealed tube. These experiments show that *sulphuric acid contains hydrogen, sulphur and oxygen.*

(iv) **Affinity for water.**—Miscible with water in all proportions, concentrated sulphuric acid has great affinity for water. Much heat is evolved when the acid is mixed with water, forming the hydrates :

$$H_2SO_4, H_2O\ ;\ H_2SO_4, 2H_2O\ ;\ \text{and}\ H_2SO_4, 4H_2O.$$

The great affinity of concentrated sulphuric acid for water is shown by its dehydrating action upon formic and oxalic acids, alcohol, sugar and starch—sugar and starch are charred by the acid with separation of carbon.

$$C_{12}H_{22}O_{11}\ \text{(sugar)} - 11H_2O = 12C\ ;\ HCOOH\ \text{(formic acid)} - H_2O = CO.$$

Concentrated sulphuric acid is used for drying gases such as oxygen, nitrogen, sulphur dioxide and chlorine on which it does not act chemically.

(v) **Acid properties.**—In aqueous solution sulphuric acid behaves as a strong acid, since it is highly ionised. $H_2SO_4 \rightleftharpoons H^+ + HSO_4'$; $HSO_4' \rightleftharpoons H^+ + SO_4''$. Ionisation takes place in two stages. A dibasic acid it forms *acid* and *normal* salts, such as $NaHSO_4$ and Na_2SO_4.

Dilute sulphuric acid usually reacts with all metals (except lead) such as iron, magnesium, zinc, etc. standing *above* hydrogen in the electro-chemical series (p. 130) liberating hydrogen and a salt of the metals but metals such as mercury, copper and silver standing *below* hydrogen in the series are not attacked by cold dilute sulphuric acid.

$H_2SO_4 + Fe$ [illegible]$_2 + FeSO_4$; $Mg + H_2SO_4 = H_2 + MgSO_4$.

At the ordinary temperature it liberates carbon dioxide from carbonates and neutralises alkalis. At higher temperature sulphuric acid displaces the stronger nitric and hydrochloric acids from their salts, since it is less volatile than these acids :

$$NaCl + H_2SO_4 \leftrightarrows NaHSO_4 + HCl\ ;\ NaNO_3 + H_2SO_4 \leftrightarrows NaHSO_4 + HNO_3.$$

(vi) **Oxidising properties.**—Hot concentrated sulphuric acid is an oxidising agent, and dissolves many metals such as zinc, lead, silver, mercury and copper, standing both *above* and *below* hydrogen in the electro-chemical series, yielding sulphur dioxide, water and a salt of the metal : $Pb + 2H_2SO_4 = PbSO_4 + 2H_2O + SO_2$.

Hot concentrated sulphuric acid oxidises sulphur to sulphur dioxide, carbon to carbon dioxide and phosphorus to phosphorous acid,

H_3PO_3. It also decomposes HBr and HI, liberating bromine and iodine respectively.

$$S+2H_2SO_4 = 2H_2O+3SO_2\ ;\ C+2H_2SO_4 = 2H_2O+CO_2+2SO_2\ ;$$
$$2HBr+H_2SO_4=2H_2O+Br_2+SO_2\ ;\ 3H_2SO_4+2P = 2H_3PO_3+3SO_2.$$

(vii) **Electrolysis of sulphuric acid** under different conditions may yield the following products : (a) hydrogen and oxygen (p. 10), (b) ozonised oxygen (p. 203), and (c) perdisulphuric acid (p. 213).

Tests.—Heated with copper turnings, concentrated sulphuric acid evolves sulphur dioxide, recognisable by the smell of burning sulphur. With barium chloride solution dilute sulphuric acid gives a white crystalline precipitate of barium sulphate, insoluble in concentrated hydrochloric acid.

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

A small quantity of a sulphate, $ZnSO_4$ for example, is fused on charcoal with sodium carbonate—the fused mass is then treated with dilute HCl and covered with a lead acetate paper which turns black. The reaction depends upon the formation of sulphide : $ZnSO_4 + 4C = ZnS + 4CO$. *This test detects sulphur in a sulphate.*

Uses.—Sulphuric acid is used in innumerable chemical industries—its consumption is indeed an index of industrial progress of a country. It is used (i) in the manufacture of hydrochloric and nitric acids, paints, pigments, dyes, glue and explosives, (ii) in the preparation of alum, fertilisers such as ammonium sulphate and superphosphate of lime, glucose from starch and (iii) in steel-pickling and galvanisation, in the refining of petroleum, in the parting of gold and silver, in textile industry, and in storage batteries—to mention but a few applications of the acid. Oleum is used in sulphonation reactions in organic chemistry.

The chlorides of sulphuric acid.—By the action of phosphorus pentachloride on concentrated sulphuric acid one or both hydroxyl groups may be replaced by chlorine, forming *chlorosulphonic acid* and *sulphuryl chloride :*

$$SO_2(OH)_2 + PCl_5 = SO_2(OH)Cl + POCl_3 + HCl.$$
$$SO_2(OH)Cl + PCl_5 = SO_2Cl_2 + POCl_3 + HCl.$$

They are *liquids*, and may be separated by fractional distillation, since they have widely different boiling points ; $POCl_3$, 107.2° ; $SO_2(OH)Cl$, 151° ; SO_2Cl_2, 69.1° The chlorides of sulphuric acid are colourless fuming liquids which are decomposed by water into sulphuric and hydrochloric acids :

$$SO_2(OH)Cl + H.OH = SO_2(OH)_2 + HCl.$$
$$SO_2Cl_2 + 2H.OH = SO_2(OH)_2 + 2HCl.$$

Chlorosulphuric acid is obtained on a large scale by passing dry hydrogen chloride through fuming sulphuric acid (containing SO_3), and distilling :

$$SO_3 + HCl = SO_2(OH)Cl.$$

Sulphuryl chloride is prepared by direct union of chlorine and sulphur dioxide in presence of sunlight or animal charcoal ; $SO_2 + Cl_2 = SO_2Cl_2$; also by heating chlorosulphonic acid in presence of mercuric sulphate which acts as a catalyst :

$$2SO_2(OH)Cl = SO_2Cl_2 + H_2SO_4.$$

Sodium thiosulphate, $Na_2S_2O_3$, is obtained : (i) by boiling finely powdered sulphur with sodium sulphite solution :

$$Na_2SO_3 + S = Na_2S_2O_3.$$

On evaporating the filtered solution and cooling, the salt separates in colourless monoclinic crystals, $Na_2S_2O_3$, $5H_2O$. It is used in photography and commonly called 'hypo'.

The sodium sulphite is made by neutralising sodium bisulphite with sodium carbonate—the sodium bisulphite is first obtained by passing sulphur dioxide into sodium carbonate solution.

$$Na_2CO_3 + 2SO_2 + H_2O = 2NaHSO_3 + CO_2.$$

$$2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + H_2O + CO_2.$$

(ii) by passing sulphur dioxide into sodium sulphide solution—the 'mother liquor' left after the crystallisation of sodium sulphide which is produced by roasting salt cake with coke : $Na_2SO_4 + 4C = Na_2S + 4CO$, is a commercial source for sodium sulphide. $3SO_2 + 2Na_2S = 2Na_2S_2O_3 + S$.

$$2Na_2S + Na_2CO_3 + 4SO_2 = 3Na_2S_2O_3 + CO_2.$$

A thiosulphate is produced as well as a sulphide or poly-sulphide when sulphur is boiled with caustic alkali or milk of lime.

$$6NaOH + 4S = Na_2S_2O_3 + 2Na_2S + 3H_2O.$$

When iodine acts on a mixture of sodium sulphite and sulphide, thiosulphate results :

$$Na_2SO_3 + Na_2S + I_2 = Na_2S_2O_3 + 2NaI.$$

Sodium thiosulphate crystals melt at 48° ; on heating the salt loses water at 215°, and decomposes above 223°.

$$4Na_2S_2O_3 = 3Na_2SO_4 + Na_2S_5.$$

On adding dilute acid to a solution of sodium thiosulphate free unstable *thiosulphuric acid* (unknown in the pure state) is perhaps formed but readily decomposes into sulphur dioxide and sulphur. which deposit as a white turbidity : $H_2S_2O_3 = H_2O + SO_2 + S$.

Sodium thiosulphate dissolves silver chloride, bromide and iodide, forming sodium silver thiosulphate, and hence its use in 'fixing in photography' : $2Na_2S_2O_3 + AgBr = Na_3[Ag(S_2O_3)_2] + NaBr$.

Sodium thiosulphate solution reacts with silver nitrate forming a white precipitate of silver thiosulphate, which readily turns yellow, then brown and finally black, depositing silver sulphide :

$$Na_2S_2O_3 + 2AgNO_3 = Ag_2S_2O_3 + 2NaNO_3 ;$$

$$Ag_2S_2O_3 + H_2O = H_2SO_4 + Ag_2S.$$

When ferric chloride solution is gradually added to sodium thiosulphate, there is at first a *purple colour* due to ferric thiosulphate, and then the solution becomes colourless as the iron is reduced to the ferrous state :

$$3Na_2S_2O_3 + 2FeCl_3 \rightleftharpoons Fe_2(S_2O_3)_3 + 6NaCl.$$

$$2Na_2S_2O_3 + 2FeCl_3 = 2FeCl_2 + 2NaCl + Na_2S_4O_6.$$

On adding sodium thiosulphate to a brown solution of iodine in potassium iodide, the brown colour is discharged and sodium tetrathionate is formed—the reaction is quantitative and is used in *iodometry* : $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$.

Thiosulphate is oxidised by chlorine or bromine water :

$$Na_2S_2O_3 + Cl_2 + H_2O = Na_2SO_4 + 2HCl + S.$$

With excess of chlorine, the sulphur is oxidised to sulphuric acid :

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O = Na_2SO_4 + 8HCl + H_2SO_4.$$

Potassium permanganate in *neutral* solution oxidises thiosulphate to sulphate : $2KMnO_4 + Na_2S_2O_3 = K_2SO_4 + Na_2SO_4 + Mn_2O_3$.

Sodium thiosulphate is used as : (i) an analytical reagent in the laboratory ; (ii) an *antichlor* to remove chlorine from bleached fabrics, (iii) a 'fixer' in photography, and (iv) in the extraction of gold and silver in the lixiviation process.

Exercises

1. Mention the principal sources of sulphur and briefly describe the method for its extraction : (i) from surface deposits, (ii) from underground deposits. How would you prove that a sulphate contains sulphur ?

Under what conditions does sulphur react with (a) caustic soda, (b) iron (c) coke, (d) chlorine, and (e) concentrated sulphuric acid ?

2. Give a brief account of the allotropy of sulphur. Describe the changes that may be observed when sulphur is gradually heated to its boiling point. How would you convert sulphur into (a) hydrogen sulphide, (b) sodium bisulphite, and (c) sodium thiosulphate ? *Punjab Inter.*

3. How is hydrogen sulphide prepared and purified in the laboratory ? How would you prove that (a) the gas contains hydrogen and sulphur, (b) its molecular formula is H_2S ? Describe the action of the gas on solution of : (a) ferric chloride, (b) lead nitrate, (c) sulphur dioxide, and (d) zinc sulphate. *Calcutta '53*

4. How would you collect and purify a specimen of hydrogen sulphide ? How would you show experimentally that the gas is (a) a reducing agent, (b) a very weak dibasic acid ? Explain why dilute sulphuric acid and not nitric acid is used for preparing hydrogen sulphide. Describe the reaction of the gas with (a) dilute nitric acid, (b) concentrated sulphuric acid, (c) iodine suspended in water, and (d) zinc sulphate. *Delhi '37*

5. Describe the preparation of pure and dry sulphur dioxide. What reactions take place when the gas is led into : (a) chlorine water, (b) caustic potash solution, (c) a mixture of nitrogen dioxide and water vapour, (d) cupric chloride, and (e) hydrogen sulphide ? Explain how it behaves both as an oxidising and as a reducing agent. *U. P. Board '51*

6. How would you prove experimentally that sulphur dioxide contains sulphur, and its own volume of oxygen ? State how it reacts with (a) nitric acid, (b) lead dioxide, (c) sodium carbonate, (d) milk of lime, and (c) potassium permanganate. *Calcutta Inter.*

7. How is sulphuric acid manufactured by the lead chamber process ? How would you imitate the process in the laboratory ? Outline the principal uses of the acid. *Calcutta '54*

8. Describe the manufacture of sulphuric acid by the contact process. What advantages does this process possess over the lead chamber process ? How would you show that sulphuric acid contains hydrogen, oxygen and sulphur ? *Calcutta '47*

9. Describe experiments to show that sulphuric acid acts as (i) an acid, (ii) a dehydrating agent, (iii) an oxidising agent. Describe the action of the acid upon ; (a) sulphur, (b) lead, (c) potassium bromide, (d) a mixture of calcium fluoride and sand, (e) common salt, (f) oxalic acid.

10. Explain how you would distinguish between (i) a soluble sulphate and sulphide, (ii) chlorine and sulphur dioxide. *Calcutta '57*

11. Explain what happens when : (a) the gaseous product obtained by heating pyrites is led into a solution of potash, (b) hydrogen sulphide is passed into an alkaline solution of zinc sulphate, (c) a mixture of sulphur dioxide and air is gradually added to a mixture of ferrous sulphate and dilute nitric acid ?

XXIII

Carbon

Symbol C. Atomic weight 12.010. Atomic number 6.

Occurrence.—Elementary carbon occurs in nature as *diamond* and *graphite*. It is present in air as carbon dioxide (about 3 volumes in 10,000) and as carbonate in sedimentary rocks such as *limestone* and *dolomite*. An essential constituent of all animal and vegetable bodies, it is found as *carbohydrates* such as starch, sugar and cellulose, all occurring in plants, and as *proteins*, such as albumin and gelatin, occurring both in plants and animals. It is present in petroleum as *hydrocarbons*. Coal is a carbonaceous mineral of vegetable origin.

The Allotropy of carbon.—The different crystalline and amorphous allotropes of carbon are :

(i) *crystalline : diamond* and *graphite ;*

(ii) *amorphous : charcoal, lampblack* (or *soot*), *coke, gas carbon,*

Graphite is the stablest form of carbon. The amorphous carbon has been shown by X-ray analysis to be micro-crystalline graphite in structure.

The identity of the allotropic forms of carbon, such as diamond, graphite and charcoal, is established by burning equal weights of the three varieties in a current of pure and dry oxygen and absorbing the carbon dioxide formed in previously weighed tubes containing caustic potash when equal weights of the same product carbon dioxide are obtained. $C + O_2 = CO_2$.

About 0.5 g. of an allotrope of carbon is weighed out in a porcelain boat which is then placed in a hard glass tube C (fig. 124). The carbon is gently heated in a current of pure and dry oxygen (which is bubbled through strong sulphuric acid in A and thereby dried), and the carbon dioxide formed absorbed in the previously weighed potash tubes B.

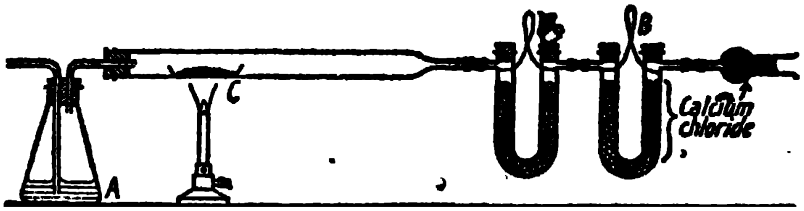


Fig. 124

Diamond.—It occurs naturally in Goleconda in India, South Africa, Brazil, the Ural mountain and elsewhere. South African mines alone supply over 90% deposits, and are separated by washing.

Diamonds are rated in *carats*—one *carat* = 0.2054 gm. ; the International carat = 0.200 gm. The world-famous gem *Kohinoor* originally weighed 186 carats, but had to be cut to 106 carats. Other famous diamonds are the *Hope* (44.5 carats), the *Cullinan* (3032 carats), and the Pitt (136.25 carats).

Properties.—(i) Diamond forms transparent lustrous crystals of high refractive index 2.42, for light—colourless, diamonds are almost pure carbon. Transparent diamonds are occssionally pink, green or blue.

(ii) It is the densest form of carbon with a specific gravity 3.52 and is a non-conductor of heat and electricity. It is transparent to X-rays —the imitation diamond (made of glass) is opaque to the rays.

(iii) Diamond is extremely hard and is not scratched by any substance (except) boron carbide B_4C) and heads Mohs **scale of hardness** :

1. *Talc*
2. *Gypsum*
3. *Calcite*
4. *Fluorite*
5. *Apatite*
6. *Orthoclase*
7. *Quartz*
8. *Topaz*
9. *Corundum*
10. *Diamond*

Each mineral in the scale is scratched by all others below it. Diamond is about 140 times harder than corundum.

(iv) Very inert chemically, it is not attacked by acids, alkalis or fused potassium chlorate.

Artificial diamond.—It was prepared by Moissan in 1893 by heating sugar charcoal with iron in a carbon crucible to a temperature of above 3000°C by means of an electric arc furnace—molten iron dissolving the charcoal, and then *suddenly* cooling the solution by immersion in molten lead—carbon separates as very fine crystals of diamond which are freed from iron by dissolving out the latter with hydrochloric acid. Graphite separates on *slow* and *gradual* cooling. The process could not be commercially exploited owing to the microscopic size of the crystals produced.

Uses of diamond.—Diamonds are generally cut for gems and also used, on account of their extreme hardness, for cutting glass and for rock-boring purposes. The opaque and black diamonds known as *carbonado* and *bort,* being less valuable, *are usually used for rock-drilling, and also for cutting and polishing diamonds and stones. Diamonds can be cut only by other diamonds.*

Graphite.—Graphite (*grapho,* I write), also called **plumbago** or **black lead,** is found in Ceylon, Siberia, Bohemia, California and elsewhere.

Properties.—(i) Unlike diamond, graphite is opaque, *soft* and greasy to the touch with an almost *metallic lustre* and *conducts heat and electricity ;* it is also less dense—its specific gravity is 2.25.

(ii) Like diamond, graphite is crystalline—their crystalline forms are different, graphite having hexagonal and diamond tetrahedral arrangement of the carbon atoms in the crystals. Grey, flaky hexagonal crystals of graphite easily mark paper, and hence the use of graphite in the so-called *lead-pencils.*

(iii) Slightly more reactive than diamond, graphite is oxidised to CO_2 in air at 700°, and to CF_4 in fluorine at 500°. Though unattacked by dilute acids, caustic alkalis or chlorine, it is slowly oxidised to CO_2 by chromic acid, and to CO by fused sodium carbonate.

(iv) Unlike diamond, it is oxidised below 100° to a yellow insoluble solid, *graphitic-acid,* $C_{11}H_4O_5$' which breaks down into *mellitic acid* $C_6(COOH)_6$ (a derivative of benzene) by a mixture of concentrated sulphuric and nitric acids and potassium chlorate. *Formation of graphitic acid is regarded as a test for graphite.*

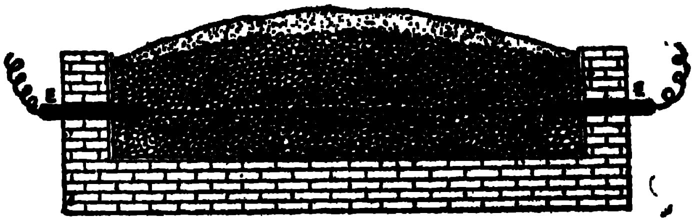


Fig. 125

Artificial graphite.—Artificial graphite is manufactured by the **Acheson process** at Niagara in which a mixture of sand and powdered petroleum coke is strongly heated for about 25-30 hours to a very high temperature between 2500°C and 3000°C by means of electric current led into the mixture by carbon rods embedded in the mass—the mixture is being supported on a brick-furnace and covered with sand (fig. 125). Sand and carbon react, yielding silicon carbide which then decomposes, depositing graphite, and silicon which latter volatilises away.

$$SiO_2 + 3C = SiC + 2CO \; ; \quad SiC = Si + C.$$

Uses of graphite.—(*i*) Graphite is used in making so-called *lead pencils*, and for *polishing iron stoves*, (*ii*) Colloidal graphite as a suspension in oil is used in *lubricating* machinery, (*iii*) Since it conducts electricity, it is used in making electrodes and *heating elements* in electric furnaces, and for coating articles of non-conducting materials meants for *electro-typing*, (*iv*) Mixed with clay, it is used in making *plumbago crucibles* which combine refractory properties with thermal conductivity.

Amorphous carbon.—Charcoals : There are different varieties of charcoal, depending upon the source, such as wood charcoal, sugar charcoal, and animal charcoal.

(i) **Wood charcoal.**—This is made by the dry distillation of wood in externally heated iron retorts (fig. 126) from which air is excluded. The products of distillation are (a) the inflammable gas, known as *wood gas*, used for heating the retorts, (b) the volatile liquid distillate, consisting of *wood tar* and an aqueous portion, called *pyroligneous acid* which contains acetic acid, methyl alcohol and acetone, and (c) the solid residue of *wood charcoal* in the retort. Average yield : wood charcoal 25%, wood gas 25%, pyroligeneous acid 40%, and wood tar 10%.

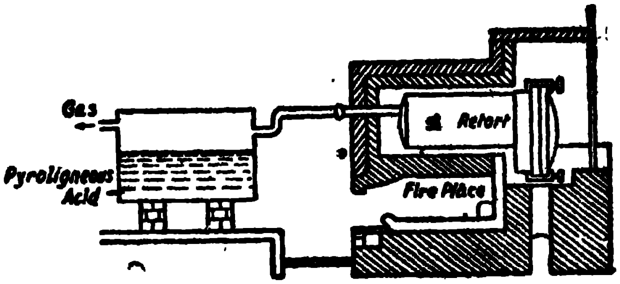


Fig. 126

Wood tar finds use as a fuel ; on refining it gives *wood oil* (a solvent), *creosote oil* (wood preservative), *guaicol* (a medicinal product) and *pitch*.

There is a wood distillation plant at Bhadrabati in the Mysore State.

In the primitive process, still in use, piles of wood are covered with earth to hinder the admission of air and lighted at the bottom—by the slow burning of a part of wood, the remainder is converted to charcoal. This is a wasteful process, since the volatile products are lost.

(ii) **Sugar charcoal.**—This is obtained by heating pure cane sugar in a covered vessel till no more gas is evolved—the resulting charcoal is then heated to 1000°C in a graphite tube in a current of chlorine to remove the residual combined hydrogen as hydrogen chloride. It is next washed with water and dried in a current of hydrogen to remove chlorine. *Sugar charcoal is the purest form of carbon.*

It may also be obtained by the action of strong sulphuric acid upon a concentrated cane sugar solution—charcoal separating as a black mass is washed with water, filtered and dried.

$$C_{12}H_{22}O_{11} \text{ (cane sugar)} = 12C + 11H_2O.$$

(iii) **Animal Charcoal (bone charcoal or bone black).**—This is made by the destructive distillation of bones in closed retorts—the volatile products distilling over condense into: (a) an alkaline watery liquid containing ammonia and nitrogenous organic bases, and (b) *bone oil* or *Dippel's oil* containing pyridine, etc. The black residue in the retort containing about 10 per cent carbon deposited on a porous framework of 90% calcium phosphate and calcium carbonate, etc., is known as *animal charcoal.* The charcoal that remains after dissolving out the calcium salts with hydrochloric acid is known as **ivory black.**

Blood on charring by similar treatment yields *blood charcoal.*

Cocoanut shells on being heated in absence of air yields an active form of charcoal. **Activated charcoal** is obtained by carbonising wood previously impregnated with zinc or magnesium chloride. It may also be made by heating wood charcoal prepared at 850°—900° in a current of steam, when the material (inactive graphite layer on the surface) obstructing the pores is removed. **Norit** is a variety of active charcoal.

Properties of charcoal.—(i) Bad conductor of heat and electricity, charcoal is black, soft and highly *porous* substance of varying sp. gr. of about 1.4 to 1.9 ; but its density is reduced to about 0.2 by air enclosed in its pores, and hence *charcoal floats on water.*

(ii) *Because of its porosity, it readily adsorbs gases*—the adsorbed gases are released on heating. Charcoal may also adsorb dissolved substances from a solution.

Experiments.—(a) A piece of red-hot wood-charcoal is inserted into a tube of ammonia standing over mercury—mercury rises up the jar as the charcoal absorbs the gas ; the charcoal takes up about 90 times its volume of ammonia gas—the activated charcoal adsorbs a much larger volume.

(b) A hot solution of a sample of crude sugar, brown in colour, is shaken with animal charcoal and then filtered—the filtrate is the colourless solution of sugar—the colouring matter being absorbed and retained by charcoal.

(c) A dilute solution of litmus is boiled with animal charcoal and filtered—the filtrate runs through colourless ; the litmus is being adsorbed by the charcoal.

Similar experiment may be done with indigo solution. Activated charcoal is a better adsorbent than ordinary charcoal.

(iii) Insoluble in water, alkalis and non-oxidising acids, charcoal is resistant to the action of chlorine, bromine, and iodine ; but unlike diamond and graphite it is oxidised to CO_2 by hot conc. H_2SO_4 ; a small amount of mellitic acid is produced at the same time. It is also oxidised by hot conc. HNO_3.

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O\ ;$$
$$C + 4HNO_3 = CO_2 + 4NO_2 + 2H_2O.$$

(iv) Charcoal ignites in oxygen a little above 400°C, whereas graphite burns at 700° and diamond at 800°. It ignites spontaneously in fluorine, yielding CF_4, while graphite burns at 500° and diamond at 700°.

(v) *Charcoal is a good reducing agent at high temperatures.* It reduces many metallic oxides such as CuO, PbO, Fe_2O_3, ZnO and SnO_2 to the respective metals ; thus copper oxide is reduced to a red mass of metallic copper on being heated with charcoal powder. Red hot charcoal reduces steam to hydrogen, and carbon dioxide to carbon monoxide.

$$CuO+C = Cu+CO\ ;\ H_2O+C = H_2+CO\ ;\ CO_2+C = 2CO.$$

(vi) Carbon combines with hydrogen at high temperature and pressure yielding methane in very small amounts ; acetylene is formed if a spark is passed between carbon electrodes in hydrogen. Carbon combines with sulphur vapour, giving carbon disulphide. $C + 2S = CS_2$; $2C + H_2 = C_2H_2$.

Uses of charcoal.—Wood charcoal is used as a fuel and as a reducing agent, in making filter-beds and gun-powder. It is very often used in sewers and hospitals to remove obnoxious gases by adsorption.

(*ii*) Animal charcoal is extensively used in the refining of sugar ; ivory black is used as a pigment.

(*iii*) Activated charcoal is used in making gas-masks.

Lamp black.—It is a fine variety of soot, prepared by burning substances rich in carbon such as kerosene, tar, turpentine and rosin, in a limited supply of air, and collecting the soot by deposition on cold surfaces—the smoke is conveyed into a chamber where it is deposited on wet suspended blankets and is subsequently removed. A fine variety, known as *gas black*, is prepared from natural gas which is methane mainly. It is a bad conductor of heat and electricity.

It is used in making printer's ink, black paint and boot-polish and in vulcanizing rubber. Lamp black contains some oily impurities which can be removed by heating in chlorine.

Coal.—Coal is a carbonaceous mineral of vegetable origin. It is the final result of a series of slow decompositions of vegetable matter of very remote past, in presence of a limited supply of air and under high pressure due to the weight of superimposed strata, in the womb of the earth. Various stages of decomposition are represented by :

Peat, lignite or brown coal, bituminous coal and anthracite.

Each step of conversion is followed by an increase in the percentage of carbon in the residue, with the corresponding increase in calorific value, expressed in B.Th.U. per pound, as the table shows : The vegetable origin of coal is disclosed by microscopic examination as well as by the presence of fossilized plants.

		Carbon	Hydrogen	Oxygen	Calorific value
Wood ...	...	50.0	6.0	44.0	7,400
Peat ...	...	60.0	5.9	34.1	9,900
Lignite ...	...	67.0	5.2	27.8	11,700
Bituminous coal	...	88.4	5.6	6.0	14,950
Anthracite ...	...	94.1	3.4	2.5	15,720

In course of decomposition, a portion of the carbon, hydrogen and oxygen is eliminated as carbon-dioxide, water and methane, and the residue becomes increasingly rich in carbon. On burning coal leaves an incombustible residue, called **ash**—the ash content of high grade coals is low, about 5 per cent or so but it may be even 25-30 per cent in low grade coals. Coal often contains sulphur (Assam coal) which may be recovered.

Bituminous coals i.e., common coals, burn with a smoky flame and are sub-divided into *caking* and *non-caking* coals, according as they do or do not soften and fuse on burning or coking. Anthracite coal does not burn with a flame and gives little smoke. Coal is extensively used as a fuel and in the manufacture of coal gas and liquid fuels.

Coke and gas carbon.—They are the by-products of coal gas industry. Very hard and compact, coke is used as a reducing agent in metallurgy. It is also used as a fuel. Coke is a bad conductor of heat and electricity.

Gas carbon is obtained as a hard deposit on the hot walls of the retorts by the thermal decomposition of hydrocarbons during the manufacture of coal gas. A good conductor of heat and electricity, it is used in making *electrodes* for arc-lights and electric *batteries*, and brushes for motors and dynamos.

Properties of different froms of carbon.—

Property	Diamond	Graphite	Amorphous carbon
1. Colour and appearance etc.	Colourless transparent crystals, high refractive index and brilliant lustre.	Greyish-black crystals, metallic lustre.	Black amorphous. ...
2. Specific gravity.	3.5	2.25	Charcoal 1.4 to 1.9 ; gas caron 2.35.
3. Hardness ; porosity.	Extremely hard but fairly brittle.	Extremely soft, greasy to touch, marks paper.	Charcoal : soft and porous ; soot : light, finely divided ; coke: hard and soft ; gas carbon : hard ; soft bituminous coal and hard anthracite.
4. Electrical conductivity	Bad conductor.	Good conductor.	Bad conductor except gas carbon which is a good conductor.
5. Adsorbing power of gas, etc.	—	—	Charcoal alone is a decoloriser, de-odoriser ; adsorbs gases.
6. Effect of heat.	Forms graphite at 1800°.	Stable form at high temperature	Changes to graphite at high temperature.
7. Burns with flame in oxygen.	CO_2 at 800°—850° ; high ignition temperature.	CO_2 at 690°C.	CO_2 at 345°C (wood charcoal) ; low ignition temperature.
8. Reacts with fluorine.	CF_4 at 700°C.	CF_4 at 500°C.	Ignites spontaneously to CF_4.

9. *Source and method of preparation* : Diamond and graphite occur in nature. Wood charcoal—destructive distillation ; animal charcoal—destructive distillation of bone and blood ; lampblack—burning petroleum and kerosene, etc. ; coke and gas carbon—destructive distillation of coal ; anthracite occurs in nature.

10. *Uses* : *Diamond* : gem, glass-cutting, rock-boring and polishing ; *Graphite* : lubricant, polishing, lead-pencils and plumbago crucibles ; *wood charcoal* : fuel, deodoriser, gunpowder, reducing agent, filtering ; *animal charcoal* ; decoloriser and sugar-refining ; *lampblack* : printer's ink, black paint, fillers for rubber ; *coke* : fuel and reducing agent ; *Gas carbon* : electrodes for arc lights and electric battery.

Oxides of carbon.—Carbon forms two important oxides namely carbon monoxide, CO, and carbon dioxide, CO_2, which are both gaseous.

Carbon dioxide, CO_2

Critical temperature 31°C. Critical pressure 72.8 atm. Boiling point—56°C at 5.3 atm. Sublimes at —78.52°C. Solubility at 0°C 1.7 vol. in 1 vol. water.

History and occurrence.—The gas, called *gas sylvestre* by Van Helmont who discovered it in 1630, was studied by Black (1754) who gave it the name *fixed air*. But it was Lavoisier who showed it to be an oxide of carbon in 1783.

In the free state it occurs in air to the extent of 0.03% by volume. The carbon dioxide of the air is mainly produced by the combustion of fuels, decay of organic matter and respiration of animals. Fermentation of sugar also produces the gas. It occurs in many spring waters, such as Vichy waters. It issues in abundance from the fissures in earth's surface in many localities such as the Poison Valley in Java and the Grotto del Cane in Naples.

In combination it occurs as carbonates, such as chalk, limestone, magnesite, dolomite, etc.

Preparation.—Carbon dioxide is formed (i) by the direct combustion of carbon in excess of air or oxygen, (ii) by the action of dilute acid on all metallic carbonates or bi-carbonates :

$Na_2CO_3+H_2SO_4 = Na_2SO_4+H_2O+CO_2$; $NaHCO_3+HCl = NaCl + H_2O+CO_2$.

(iii) By heating all metallic carbonates (except those of alkali metals and barium) or bi-carbonates.

$$CaCO_3 = CaO + CO_2 ; \quad Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

(iv) By heating sodium or potassium bi-carbonates

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Laboratory preparation.—Carbon dioxide is usually prepared by the action of acids upon carbonates. The gas is obtained in the laboratory by the action of cold dilute hydrochloric acid upon marble (calcium carbonate) : $CaCO_3+2HCl = CaCl_2+H_2O+CO_2$.

Some marble chips are taken in a Woulfe's bottle (fig. 127) fitted with a thistle funnel and a delivery tube, and covered with water. On pouring moderately strong hydrochloric acid, quick effervescence takes place due to the evolution of the carbon dioxide—the gas may be collected over water (though it is somewhat soluble) or by the upward displacement of air, since it is $1\frac{1}{2}$ times heavier than air. The gas may be washed with water (to remove HCl vapour), dried by sulphuric acid or calcium chloride and collected over mercury.

Kipp's apparatus is charged with marble and hydrochloric acid for a ready supply of the gas.

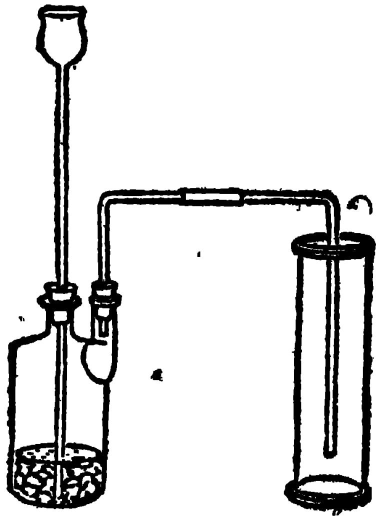


Fig. 127

Dilute sulphuric acid cannot be used with marble, since the sparingly soluble calcium sulphate produced covers the marble and soon stops the action of the acid.

Pure carbon dioxide is best obtained heating pure sodium bicarbonate : $2NaHCO_3 \rightleftharpoons Na_2CO_3 + H_2O + CO_2$.

On the industrial scale.—carbon dioxide is obtained as a by-product either in the fermentation of sugar into ethyl alcohol by the action of enzymes, present in yeast (p. 146).

$$C_6H_{12}O_6 \text{ (glucose)} = 2C_2H_5OH \text{ (alcohol)} + 2CO_2,$$

or in the production of lime by heating a mixture of limestone and coke in a kiln. The gas can also be manufactured by burning coke in excess of air :

$$CaCO_3 = CaO + CO_2 ; \quad C + O_2 = CO_2.$$

The gas is freed from nitrogen and other gases by absorption in cold potassium carbonate solution, yielding potassium bi-carbonate from which the gas is subsequently expelled by boiling. It is dried by sulphuric acid and stored in cylinders under pressure.

$$K_2CO_3 + H_2O + CO_2 \leftrightharpoons 2KHCO_3.$$

Properties.—(i) Carbon dioxide is a colourless gas with a faint pungent smell and an acid taste, easily liquefiable under pressure—at temperatures below 31°, its critical point, it may be compressed to a liquid.

(ii) The gas is not poisonous but it does not support respiration, since animals feel suffocated in its atmosphere for want of oxvgen.

(iii) The gas is 1½ times heavier than air.

The gas is poured from one jar to another just as water is poured—on adding lime water to the lower jar, it turns milky, showing that the gas is heavier than air. A soap bubble (containing air) floats on the surface of the heavier gas carbon dioxide.

(iv) It is fairly soluble in water—water dissolving its own volume of the gas at 15° ; the gas is completely expelled on boiling the solution. The solution is acidic due to the formation of *unstable carbonic acid, known only in solution* : $H_2O + CO_2 \rightleftharpoons H_2CO_3$. The solubility of the gas increases under pressure.

Carbon dioxide is passed into blue litmus solution—it turns dull red. The blue colour is restored on boiling—carbon dioxide being removed. Hence the solution of the gas is a weak unstable acid.

(v) The gas does neither burn nor supports combustion, and hence its use as a fire extinguisher. *But ignited Na, K and Mg burn in the gas with separation of carbon.*

$$4K + 3CO_2 = 2K_2CO_3 + C \; ; \; CO_2 + 2Mg = C + 2MgO.$$

A piece of burning magnesium is inserted into a jar of carbon dioxide, it continues burning with separation of soot ; when shaken with dilute HCl, magnesium oxide dissolves, black particles of carbon are seen floating in the liquid. The experiment shows the presence of carbon in carbon dioxide.

(vi) The gas may be reduced to carbon monoxide passing over red hot carbon, iron or zinc :

$$CO_2 + C = 2CO \; ; \qquad CO_2 + Fe = CO + FeO.$$

(vii) An acidic oxide, the gas reacts with bases and alkalis, yielding carbonates :

$$CaO + CO_2 \rightleftharpoons CaCO_3 \; ; \; Na_2O + CO_2 = Na_2CO_3.$$

Expt.—(*a*) **Action on lime water** :—Carbon dioxide is passed into lime water —it turns milky due to the formation of white insoluble calcium carbonate. The milkiness disappears on continued passing of the gas owing to the formation of soluble calcium bicarbonate. The milkiness appears on boiling the solution, since the bicarbonate decomposes, yielding the carbonate back.

$$CO_2 + Ca(OH)_2 = CaCO_3 \text{ (insoluble)} + H_2O$$
$$CaCO_3 + H_2O + CO_2 \leftrightharpoons Ca(HCO_3)_2 \text{ (soluble).}$$

(*b*) The gas reacts with caustic soda, giving a solution of sodium carbonate, but with excess of the gas *sparingly* soluble sodium bicarbonate is produced, which on heating gives pure carbon dioxide.

$$2NaOH + CO_2 = Na_2CO_3 + H_2O \; ; \; Na_2CO_3 + H_2O + CO_2 \leftrightharpoons 2NaHCO_3.$$

(viii) The gas is decomposed by the green colouring matter of plants, known as *chlorophyll*, in presence of sunlight and moisture into carbon, which is assimilated by plants, and oxygen which is set free (fig. 128). The process is known as *photosynthesis*.

Test.—Like nitrogen, the gas does neither burn, nor supports combustion ; but unlike nitrogen, it turns lime water milky.

Uses.—(*i*) In the manufacture of sodium carbonate by Solvay's process ; urea and salicylic acid, and in the refining of sugar.

(*ii*) As a refrigerant as **dry ice** (also called (**dri-cold**), it is so called, since it does not melt to water, as ice does, but evaporates. Carbon dioxide is liquified under a pressure of 1000 lbs. per sq. in.—the liquid on evaporation solidifies to 'carbon dioxide snow', called *dry ice* which is used for cooling ice creams, packing fish, etc. The dry ice sublimes at −79°. Liquid carbon dioxide is sold in steel cylinders.

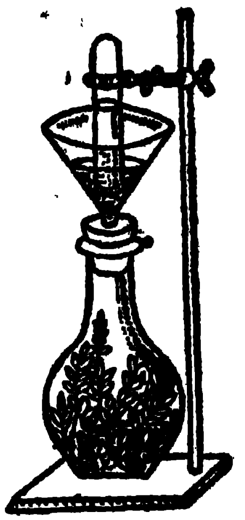


Fig. 128

(*iii*) In extinguishing fire. A **fire extinguisher** (fig. 129) consists of a metal casing B containing a solution of sodium carbonate, with a glass bottle T of sulphuric acid inside. The bottle may be broken by a rod attached to a knob H outside—the acid coming in contact with the carbonate liberates carbon dioxide which is directed against fire from a nozzle. In extinguishing oil fires carbon dioxide is used in a mixture called *foamite*. Foamite is a solution of alum or aluminium sulphate mixed with sodium bicarbonate and a sticky material such as licorice extract. Aluminium sulphate on hydrolysis produces sulphuric acid which acts on $NaHCO_3$ to form CO_2. The evolved CO_2 expands the whole mass into a thick foam which spreads over the burning oil like a blanket and shuts off oxygen.

$$Al_2(SO_4)_3+6NaHCO_3 = 2Al(OH)_3+3Na_2SO_4+6CO_2.$$

(*iv*) In the preparation of 'aerated waters' such as lemonade and soda water which are solutions of carbon dioxide under pressure ; and as a leavening agent. *Baking powder* contains sodium bicarbonate and tartaric acid, which do not react when dry. In presence of water, sodium tartrate is formed and CO_2 is evolved, the bubbles of which are expanded by heat on baking.

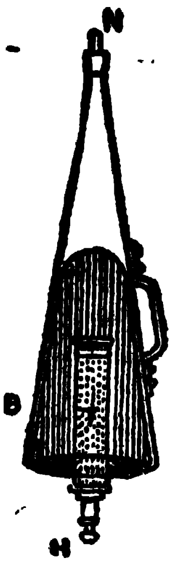


Fig. 129

(*v*) In medicine and first aid in case of shock, gas poisoning and asphyxiation. A mixture 95 per cent O_2 and 5 per cent CO_2 is administered by gas mask and forced respiration in order to stimulate natural respiration.

Composition of carbon dioxide.—(i) **By weight :** The gravimetric composition of carbon dioxide is determined by burning a known weight of pure sugar charcoal in oxygen and absorbing the carbon dioxide formed in strong caustic potash solution.

About 1 g. of pure charcoal is weighed into a tiny porcelain boat and placed inside a hard glass tube (fig. 130) one half of which is packed with granular copper oxide. The tube is then laid in a combustion furnace. The copper oxide is first heated to redness and then a *slow* stream of oxygen (first purified by passing through tube, B, containing sticks of caustic potash to remove moisture and carbon dioxide) is passed through the tube, and finally the boat containing the carbon is heated. The carbon is oxidised to carbon dioxide. Any carbon monoxide formed is converted to carbon dioxide by the hot copper oxide.

After the combustion is over, oxygen is allowed to pass through the tube to sweep out all the carbon dioxide, which is absorbed in weighed potash bulbs, and then the oxygen is displaced by air. The potash bulbs (containing strong caustic potash solution) together with the calcium chloride tube (to prevent loss of moisture from the bulbs) are weighed before and after the experiment.

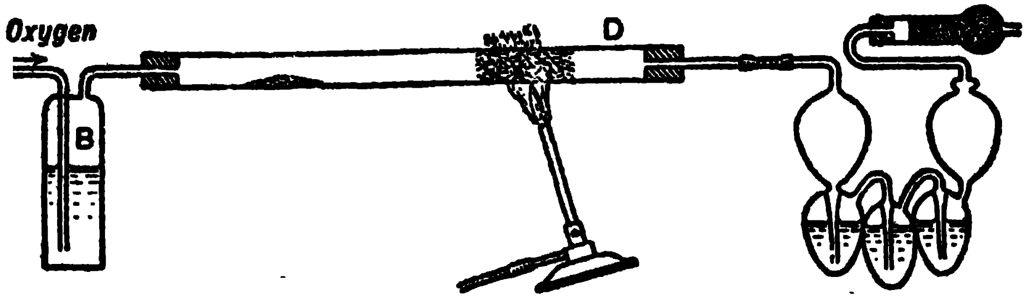


Fig. 130

Let x = weight of carbon and y = increase in weight of potash bulbs, then the weight of oxygen combined with x *of carbon* $= y - x$. Hence the percentage of carbon and oxygen in carbon dioxide may be found out—actual experiments give the following data C = 27.27 and O = 72.73. Therefore the ratio of:

$$\frac{\text{atoms of carbon}}{\text{atoms of oxygen}} = \frac{27.27/12}{72.73/16} = \frac{2.27}{4.54} = \frac{1}{2}.$$

∴ the empirical formula for carbon dioxide is CO_2.

This accords with the mol. wt. 44, vapour density being 22. Therefore the molecular formula of carbon dioxide is CO_2.

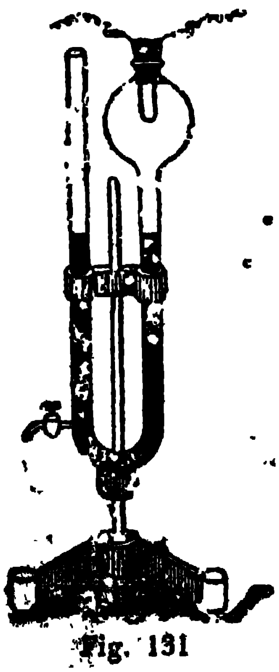


Fig. 131

(ii) **By volume**: The volumetric composition of the gas is established by burning a piece of pure sugar carcoal in a confined volume of oxygen over mercury—the experiment showing that carbon dioxide contains it own volume of oxygen. The apparatus consists of a U-tube (fig. 134) ending in a bulb at one end, which is provided with a glass-stopper through which pass two copper wires, one of which ends in a metal spoon. The two wires are connected by a platinum spiral, touching a piece of pure sugar charcoal on the spoon. The bulb and a part of the limb is filled with oxygen at atmospheric pressure by the displacement of mercury, and the charcoal is ignited by passing electric current through the spiral. Carbon is burnt into carbon dioxide. On cooling the apparatus, mercury is found to stand at the same level as before, i.e., no change in volume has taken place in the conversion of carbon into carbon dioxide. Hence *carbon dioxide contains its own* *volume of oxygen*, i.e. 1 volume of carbon dioxide contains 1 volume of oxygen. Therefore :

1 molecule of the gas contains 1 molecule (*i.e.*, 2 atoms) of oxygen (by Avogadro's hypothesis). Hence the formula is CxO_2 and the molecular weight $= 12x+2\times16$. But the mol. wt. is 44, its density being 22, found experimentally *i.e.*, $12x+2\times16 = 44$. $\therefore\ x = 1$ and the formula of carbon dioxide is CO_2.

Carbon Monoxide, CO

Critical tem.—138.7°C ; Critical pr. 34.6 atm. ; m.p.—191.5°C ; m.p.—200°C.

Formation.—Carbon monoxide was first discovered by Lassone in 1766 by heating charcoal with zinc oxide. The gas is formed (*i*) by the incomplete combustion of carbon in limited supply of air or oxygen. (*ii*) by heating charcoal with oxides of zinc or iron, or with chalk :

$$ZnO + C = Zn + CO, \qquad CaCO_3 + C = CaO + 2CO.$$

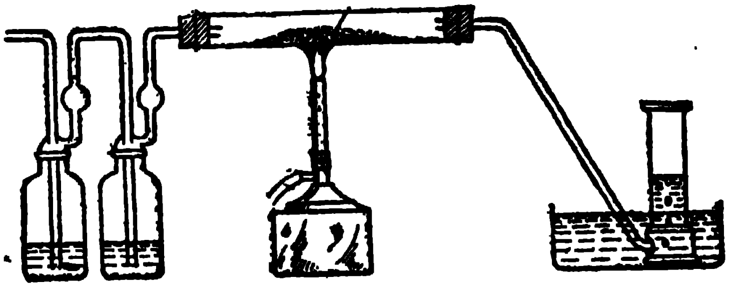


Fig. 132

(*iii*) by the reduction of carbon dioxide by passing a slow stream of the gases over red-hot charcoal, iron or zinc. Carbon dioxide is first dried by passing through concentrated sulphuric acid and then slowly led over a layer of charcoal heated to redness in an iron tube (fig. 132)—the resulting CO is collected over strong caustic potash solution, which absorbs the unreduced CO_2.

$$CO_2 + C \leftrightharpoons 2CO \ ; \ CO_2 + Zn = CO + ZnO.$$

The flickering blue flames above a coal fire is due to carbon monoxide burning to carbon dioxide. The formation of carbon monoxide in coal fire is due to the reduction of the carbon dioxide, formed in the lower part of the fire in presence of free air, to monoxide in passing upwards through the bed of red-hot charcoal in the centre of the fire.

Carbon monoxide, also called *carbonic oxide*, occurs in coal gas, water gas, in the fumes of burning charcoal and in the exhaust from motor engines.

Laboratory Preparation.—Carbon monoxide is usually prepared in the laboratory by abstracting the elements of water from either formic acid HCOOH or oxalic acid $(COOH)_2$ by the action of hot concentrated sulphuric acid. Formic acid (a liquid) is slowly added from a tap funnel into concentrated sulphuric acid in a flask (fig. 133) heated to about 100°. The carbon monoxide produced is washed with caustic potash solution to remove traces of carbon dioxide and sulphur dioxide formed by the reduction of

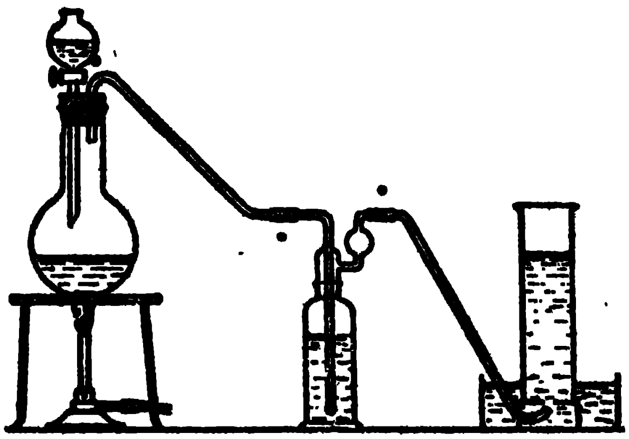


Fig. 133

sulphuric acid. $H_2SO_4 + CO = H_2O + SO_2 + CO_2$, and collected over water. The gas may also be obtained by heating sodium formate with concentrated H_2SO_4.

$$HCOOH = CO + H_2O.$$

Crystals of oxalic acid, on warming with concentrated sulphuric acid, evolve a mixture of equal volumes of carbon dioxide and carbon monoxide. The gaseous products of the reaction are passed through strong caustic potash solution to absorb carbon dioxide, the carbon monoxide is collected over water.

$$HOOC-COOH = CO + CO_2 + H_2O.$$

To obtain the gas in the pure state, it may be dried with phosphorus pentoxide and collected over mercury.

Potassium ferrocyanide on heating with concentrated sulphuric acid evolves carbon monoxide vigorously :

$$K_4Fe(CN)_6+6H_2SO_4+6H_2O = 2K_2SO_4+FeSO_4+3(NH_4)_2SO_4+6CO.$$

Properties.—(i) Carbon monoxide is a colourless gas with a peculiar faint smell and is *highly poisonous*—a concentration of less than 1% breathed continuously causes death.

Its poisoning effect is due to the fact that it combines with hæmoglobin, the oxygen carrier of the blood, forming a stable compound carboxy-hæmoglobin, and so prevents it from fulfilling its normal function in respiration. This explains why it is dangerous to burn coke in chambers insufficiently ventilated. 1 vol. of CO in 10,000 vols. of air produces symptoms of poisoning, while 1 in 300 vols. causes death in 30 minutes.

(ii) Very slightly lighter than air, the gas is sparingly soluble in water, about 3% by volume, but it freely dissolves, in either ammoniacal or hydrochloric acid solution of cuprous chloride which is the **absorbent** for the gas, forming a compound, $CuCl,CO,2H_2O$.

(iii) Non-supporter of combustion, the gas burns in air of oxygen with a *pale blue-flame*, yielding carbon dioxide : $2CO + O_2 = 2CO_2$.

(iv) *It is a powerful reducing agent ;* it reduces the oxides of such metals as lead, copper and iron at red heat—this property is made use of in many metallurgical processes.

$$PbO + CO = Pb + CO_2\ ;\quad Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

At 90°C CO reduces iodine pentoxide to iodine—the reaction is used to determine traces of CO in air. $I_2O_5 + 5CO = I_2 + 5CO_2$.

CO reduces steam in presence of mixture of heated Fe_2O_3 and Cr_2O_3 catalyst : $H_2O + CO \rightleftharpoons H_2 + CO_2$.

(v) *An unsaturated compound,* it undergoes additive reactions : thus it combines directly with chlorine in sunlight giving carbonyl chloride, also called phosgene : $CO + Cl_2 = COCl_2$. With sulphur vapour it gives carbonyl sulphide : $CO + S = COS$.

It reacts with metals like iron, cobalt and nickel at slightly elevated temperature to form metallic carbonyls which are usually volatile liquids :

$$Fe + 5CO = Fe(CO)_5 \quad Ni + 4CO \rightleftharpoons Ni(CO)_4.$$

(vi) *A neutral oxide,* it has got no action upon lime water or any alkali. But at 200°C and under pressure it reacts with a strong solution of caustic soda, yielding sodium formate :

$$CO + NaOH = HCOONa \text{ (sodium formate).}$$

Tests.—Carbon monoxide burns with a pale blue flame yielding carbon dioxide which turns lime water milky. Test papers soaked in platinum chloride or palladium chloride solution when exposed to suspected atmosphere, is turned pink, green or black due to the reduction of the chloride by carbon monoxide.

$$PdCl_2 + H_2O + CO = Pd + 2HCl + CO_2.$$

Traces of carbon monoxide in air may be detected by shaking with diluted blood, and then examining the blood spectroscopically. If carboxy hæmoglobin is present in the blood, it gives a red precipitate with tannin solution instead of the normal brown precipisate.

Uses.—It is used as a fuel in the form of producer gas and water gas, as a reducing agent, and in the extraction of nickel. Methylalcohol, CH_3OH, is obtained by passing a mixture of CO and H_2 (water gas) over a catalyst of $ZnO + Cr_2O_3$, heated to 350°C, at 200 atmospheres ; $CO + 2H_2 = CH_3OH$. The methane is formed with nickel at 380°C and at atmospheric pressure : reaction between CO and H_2 may be directed by the choice of the catalyst—$2CO + 2H_2 = CH_4 + CO_2$. The reaction between CO and H_2 in presence of iron catalyst yield synthetic liquid fuel (Fischer-Tropsch process).

Composition of carbon monoxide.—(i) **By volume :** Carbon monoxide yields only carbon dioxide when burnt in oxygen ; it is therefore a lower oxide of carbon. A known volume of carbon monoxide and a measured excess of oxygen are collected over mercury in a eudiometer at atmospheric pressure, and exploded. The explosion takes place with a contraction in volume (due to the absorption of oxygen by carbon monoxide) which is equal to half the volume of carbon monoxide taken. There is a further contraction on absorption with caustic potash—this is due to the carbon dioxide formed ; it is equal to the volume of carbon monoxide

$$C_xO_y + \tfrac{1}{2}O_2 = CO_2.$$

Hence 1 volume of carbon monoxide combines with half volume of oxygen to yield one volume of carbon dioxide. But one volume of carbon dioxide contains one volume of oxygen, of which one-half is derived from gaseous oxygen, so that the other half must be present in carbon monoxide. Hence carbon monoxide contains half its volume of oxygen. One molecule of carbon monoxide, therefore, contains ½ molecule of oxygen, by Avogadro's hypothesis. Hence the formula is C_xO and the mol. wt. $= 12x + 16$. But its mol. wt. is 28, the density is found by experiments to be 14. $\therefore\ 12x + 16 = 28$, whence $x = 1$. The formula of carbon monoxide is, therefore, CO.

(ii) **By weight :** A slow stream of pure carbon monoxide is passed through a weighed tube containing copper oxide, heated to redness in a furnace. Carbon monoxide is oxidised by hot copper oxide to carbon dioxide which is absorbed in previously weighed potash bulbs. The potash bulbs and the copper oxide tube are separately weighed after the experiment.

Let the wt. of CO_2 formed (= the increase in weight of potash bulbs) = a gm. Assuming the composition of CO_2 to be known, the weight of carbon present in this weight of $CO_2 = 12a/44$.

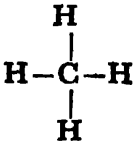
Let the weight of oxygen used (= loss in weight of CuO-tube) = b gm. The weight of carbon monoxide = $(a-b)$ gm., and the wt. of oxygen present in carbon monoxide = $[(a-b)-(12a\div44)]$ gm. Hence the percentage of carbon and oxygen in carbon monoxide may be determined—actual experiments give them to be C = 42.8 and O = 57.2. Hence the empirical formula is CO. This agree with the mol. wt. 28, the vapour density being 14. Hence the formula is CO.

Comparison of the oxides of carbon :

Properties	CO_2	CO
1. Nature, colour and smell, etc.	Colourless gas ; faint pungent smell and acid taste ; easily liquefiable under pressure.	Colourles gas ; peculiar faint smell, liquefiable at very low temperature and high pressure.

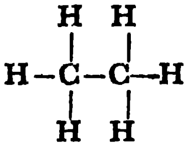
2. Density.	$1\frac{1}{2}$ times heavier than air.	Slightly lighter than air.
3. Physiological action.	Non-poisonous ; causes suffocation.	Highly poisonous.
4. Solubility in water.	Fairly soluble in water.	Very sparingly soluble.
5. Combustibility etc.	Non-combustible ; non-supporter of coubustion ordinarily, but supports combustion of ignited Mg.	Combustible—burns with a blue flame ; non-supporter of combustion.
6. Character of the oxide.	Acidic oxide ; turns blue litmus solution wine-red.	Neutral oxide ; neutral to litmus solution.
7. Action on lime water.	Lime water turns milky.	No action on lime water.
8. Action on caustic soda solution.	Forms carbonate and finally sparingly soluble sodium bicarbonate.	Forms sodium formate with caustic soda on heating and under pressure.
9. Reducing property.	Itself reduced to CO by C, Fe, etc. at red heat : $CO_2 + C = 2CO$.	Reducing agent—reduces CuO, etc. at red heat : $CuO+CO = Cu+CO_2$.
10. Additive reaction.	A saturated compound ; froms no addition product.	An unsaturated compound gives addition product with Cl_2 : $CO + Cl_2 = COCl_2$
11. Absorbent.	Caustic alkalis, usually caustic potash.	Ammoniacal solution of cuprous chloride.

The Hydrocarbons.—Carbon forms a large number of compounds with hydrogen ; they are known as hydro-carbons or hydrides of carbon. Methane, CH_4, ethane, C_2H_6, propane, C_3H_8, etc. are examples of *saturated hydro-carbons* in which the valencies of carbon atoms are *fully* satisfied. Ethylene, C_2H_4, propylene, C_3H_6, and acetylene, C_2H_2, etc., are *unsaturated hydrocarbons* in which the valencies of carbon atoms are only *partially* satisfied. Ethylene and propylene contain a double bond and acetylene a triple bond—double and triple bonds signify unsaturation. A peculiar property of a carbon atom is that it may be linked up to other carbon atoms by means of their valencies. Following structural formulæ are instructive :



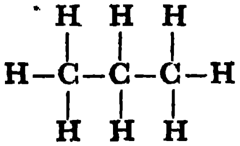
$$H-\overset{H}{\underset{H}{C}}-H$$

Methane CH_4



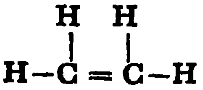
$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

Ethane C_2H_6



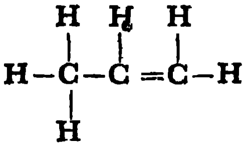
$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

Propane C_3H_8



$$H-\overset{H}{C}=\overset{H}{C}-H$$

Ethylene C_2H_4



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-H$$

Propylene C_3H_6

$H-C\equiv C-H$

Acetylene C_2H_2

Methane or marsh gas, CH_4

Boiling point—161.4° ; m.p.—185.8° ; Solubility, 5.56 volumes in 100 volumes of water at 0° ; 3.3 vols. at 20°C.

Occurrence.—Natural gas from petroleum wells contains more than 90 per cent methane. The *fire damp* of coal mine also contains this gas. Bacterial decay of vegetable matter (cellulose) at the bottom of marshy pools produces methane and hence the name *marsh gas*—the gas escapes in bubbles when the mud is disturbed. Coal gas contains about 35% methane by volume.

Methane may be synthesised : (*i*) by striking an electric arc between carbon electrodes in an atmosphere of hydrogen : $C + 2H_2 \rightleftharpoons CH_4$,

(*ii*) by passing a mixture of carbon disulphide vapour and hydrogen sulphide over heated copper : $CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S$,

(*iii*) by passing a mixture of carbon monoxide and hydrogen over nickel at about 300°C. $CO + 3H_2 = CH_4 + H_2O$.

Fairly pure methane is evolved by the action of water on aluminium carbide :

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4.$$

Preparation.—(i) Methane is prepared in the laboratory by strongly heating in a hard glass test tube or copper flask anhydrous sodium acetate with three times its weight of soda-lime. The methane is collected over water, in which it is practically insoluble :

$$CH_3COONa + NaOH = CH_4 + Na_2CO_3.$$

The anhydrous sodium acetate is made by heating the crystalline salt in a porcelain basin on a sand-bath until the water is driven off and the salt fuses. It is then cooled in a desiccator, and powdered. The sodalime is a mixture of sodium hydroxide and calcium hydroxide —its use is preferred to caustic soda alone, since it is less fusible than ~~caustic~~ soda, and does not attack glass so readily. The sodalime is made by slaking quick lime with a concentrated solution of caustic soda and drying.

Nearly pure methane is formed by heating sodium acetate with anhydrous barium hydroxide in place of sodalime.

$$2CH_3COONa + Ba(OH)_2 = 2CH_4 + BaCO_3 + Na_2CO_3.$$

Purification.—The gas prepared by this method is not pure and may contain as much as 8% hydrogen and 10% unsaturated hydrocarbons such as ethylene, etc. It is purified by passing in succession through ammoniacal cuprous chloride (to remove acetylene) and conc. H_2SO_4 (to absorb ethylene and moisture), and then collected over mercury. Thus purified methane still contains hydrogen which may be removed as water by mixing the gas with excess oxygen and passing over palladium or platinum black at 100°—the excess oxygen is then removed by alkaline pyrogallol. The methane is finally dried by concentrated sulphuric acid.

pyrogallate soln

(ii) **Pure methane**—is prepared by (a) the action of water on zinc methyl, $Zn(CH_3)_2$:

$$Zn(CH_3)_2 + 2H_2O = Zn(OH)_2 + 2CH_4.$$

(b) reducing methyl iodide by means of nascent hydrogen, liberated by the action of zinc-copper couple, (or amalgamated aluminium) on methyl alcohol.

$$CH_3I \text{ (methyl-iodide)} + 2H = CH_4 + HI$$

Zinc-copper couple is prepared by immersing granulated zinc in copper sulphate solution until coated with a layer of copper. The couple is washed with water and then with dry methyl alcohol.

The couple is taken in a flask and covered with methyl alcohol (50 c.c.) and a mixture of equal volumes of methyl iodide and methyl alcohol is slowly added from a tap-funnel (fig. 60), when methane is evolved. The gas is passed through a U-tube containing moist Zn-Cu couple to retain the accompanying methyl iodide which is very volatile, and then collected over water. The gas may be dried by conc. H_2SO_4 and collected over mercury. The Zn-Cu couple may act as follows :

$$CH_3I + Zn + CH_3OH = CH_4 + Zn(OCH_3)I.$$

(c) *Grignard reaction.*—Methyl iodide reacts with magnesium in *dry* ether medium, forming methyl magnesium iodide, which is decomposed by adding water, when pure methane is formed.

$$CH_3I + Mg = CH_3MgI$$
$$CH_3MgI + H.OH = CH_4 + Mg(OH)I.$$

Properties.—(i) A colourless gas without smell or taste and about half as light as air, methane is non-poisonous and is slightly soluble in water, but is somewhat more soluble in alcohol. Remarkable for its chemical inertness, the gas withstands the action of acids, alkalis and reducing agents.

Methane is not easily attacked by chemical reagents, and hence the name '*paraffin*' (*parum affinis* : little affinity) for the group of hydrocarbons to which it belongs.

(ii) Non-supporter of combustion, methane burns with a feebly luminous flame, yielding water vapour and carbon dioxide :

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

(iii) The gas forms an explosive mixture with air or oxygen the ignition of which causes explosion in coal mines.

The use of naked lights in coal mines brings about the ignition of methane and air, resulting in disastrous explosions.

This may be avoided by electric lighting in mines or by the use of *Davy's safety lamp* in which the flame is isolated from the surrounding atmosphere by copper gauze which by its heat conducting capacity prevents the flame from spreading to the surrounding air.

(iv) **Reaction with chlorine.**—Chlorine has no action upon methane in the dark. A mixture of methane and chlorine explodes when ignited or exposed to **bright sunlight,** giving hydrogen chloride and a black cloud of carbon. The reaction shows that methane contains carbon : $CH_4 + 2Cl_2 = C + 4HCl$, but if the mixture is exposed to **diffused sunlight,** chlorine displaces hydrogen from methane, atom by atom,—the ultimate product being carbon tetrachloride. This is a *substitution reaction :*

$$CH_4 + Cl_2 = HCl + CH_3Cl \text{ (methyl chloride).}$$
$$CH_3Cl + Cl_2 = HCl + CH_2Cl_2 \text{ (methylene chloride).}$$
$$CH_2Cl_2 + Cl_2 = HCl + CHCl_3 \text{ (chloroform).}$$
$$CHCl_3 + Cl_2 = HCl + CCl_4 \text{ (carbon tetrachloride).}$$

Methane is a saturated hydrocarbon, since all the 4 valenceis of carbon are satisfied, and, therefore, does not react with hydrogen.

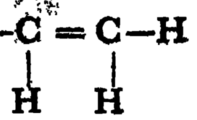
Methane also undergoes substitution with bromine, but with iodine the reaction is reversible. Methane reacts explosively with fluorine.

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI \; ; \quad CH_4 + 4F_2 = CF_4 + 4HF.$$

Uses of methane : (i) As a source of hydrogen. Methane is mixed with steam and passed over nickel supported on alumina at 725° : $CH_4 + H_2O = CO + 3H_2$. (ii) For making carbon black—methane is decomposed into carbon and hydrogen at 1000°C : $CH_4 = C + 2H_2$.

(iii) Methane is catalytically oxidised to methyl alcohol CH_3OH and formaldehyde H.CHO.

Ethylene,



$$H-\underset{\displaystyle H}{\underset{|}{C}}=\underset{\displaystyle H}{\underset{|}{C}}-H$$

Boiling point —103.7 ; m.p. —169.5°. Solubility in water, 0.163 volume in 1 vol. at 18°.

The gas was first discovered by Becher in 1669. It occurs in coal gas to the extent 4—10% by volume.

Preparation.—Ethylene is prepared : (i) by dehydrating ethyl alcohol with concentrated H_2SO_4 or phosphoric acid, or by passing the alcohol vapour over heated alumina. Ethylene or olefiant gas as it is sometimes called, is prepared in the laboratory by 'removing the elements of water' from ethyl alcohol by sulphuric acid. A mixture of about 30 c.c. of ethyl alcohol with 80 c.c. of concentrated sulphuric acid is taken in a flask fitted with a tap-funnel and a delivery tube. The flask (fig. 133) is gently heated to about 160° on a sand bath, and a mixture of equal volumes of alcohol and sulphuric acid is slowly added from the tap-funnel as the reaction proceeds. Some glass beads (or a little anhydrous aluminium sulphate) are placed in the flask to prevent frothing. The reaction takes place in two stages—ethyl hydrogen sulphate first formed decomposes into sulphuric acid and ethylene : At 140°, ~~$C_2H_5SO_4$~~

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$

$$C_2H_5HSO_4 = C_2H_4 + H_2SO_4.$$

The gas is washed with caustic potash solution to absorb carbon dioxide and sulphur dioxide (formed by the partial reduction of sulphuric acid), and then collected over water. It may be dried by calcium chloride.

Purer ethylene is obtained by dehydrating ethyl alcohol with syrupy phosphoric acid at 230°.

Preparation of ethylene dibromide.—The ethylene gas as made above is washed with caustic soda solution, and then passed into two wash-bottles containing 10 and 2 c.c.'s bromine, covered with a layer of water, respectively. The wash-bottles are well-cooled in water. Ethylene is gradually absorbed and bromine becomes paler in colour, and finally a colourless liquid, ethylene dibromide, $C_2H_4Br_2$, is obtained. The liquid is purified by shaking with Na_2CO_3 solution in a separating funnel. The lower, and therefore, the heavier ethylene dibromide layer is then separated, washed with water, and finally dried over calcium chloride and distilled. The distillate between 130-132° is ethylene dibromide.

Pure ethylene is evolved : (i) by heating ethylene dibromide with zinc dust.

$$C_2H_4 + Br_2 = C_2H_4Br_2 ; \quad C_2H_4Br_2 + Zn = ZnBr_2 + C_2H_4.$$

(ii) by heating ethyl iodide or ethyl bromide, C_2H_5Br, with an alcoholic solution of caustic potash.

$$C_2H_5I \text{ (ethyl iodide)} + KOH = C_2H_4 + KI + H_2O.$$

Ethylene is technically obtained : (i) by passing ethyl alcohol vapour over heated alumina or kaolin at about 350°C : $C_2H_5OH = C_2H_4 + H_2O$.

(ii) by cracking propane obtained from natural gas :

$$CH_3-CH_2-CH_3 \longrightarrow CH_2 = CH_2 + CH_4$$

Cracked petroleum is an important source of ethylene.

Properties.—(i) Colourless, sweet-smelling gas, ethylene is not poisonous, and has anaesthetic properties. Sparingly soluble in water, the gas is as heavy as air.

(ii) Non-supporter of combustion, the gas burns in air or oxygen—the flame in air is luminous and smoky, and in oxygen bright and smokeless. The gas forms as explosive mixture with air or oxygen :

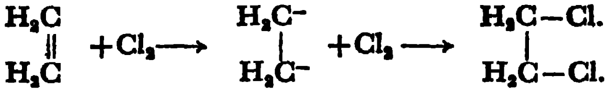
$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O,$$

(iii) **Action of chlorine.**—A mixture of ethylene and chlorine burns with a red flame, forming fumes of HCl and clouds of carbon :

$$C_2H_4 + 2Cl_2 = 2C + 4HCl.$$

but when exposed to light at ordinary temperature, an oily liquid, ethylene dichloride, also called **Dutch liquid,** is formed by direct addition*: $C_2H_4 + Cl_2 = C_2H_4Cl_2$.

* This reaction is typical of many reactions of the *unsaturated hydrocarbon* ethylene (*containing a double bond between the carbon atoms*) in which two monovalent atoms or groups are added to a molecule of ethylene, yielding a saturated additive compound. The reaction with chlorine may be formulated as :



$$\begin{matrix} H_2C \\ \| \\ H_2C \end{matrix} + Cl_2 \longrightarrow \begin{matrix} H_2C- \\ | \\ H_2C- \end{matrix} + Cl_2 \longrightarrow \begin{matrix} H_2C-Cl. \\ | \\ H_2C-Cl. \end{matrix}$$

Ethylene differs from methane in being an *unsaturated hydrocarbon ;* it forms compounds by direct addition instead of by substitution, as in the case of methane.

(iv) **Addition reactions.**—An unsaturated hydrocarbon ethylene readily forms addition compounds with :

(a) chlorine, bromine, hydrobromic acid and hydriodic acid.

When ethylene is led into bromine (a red liquid), the latter decolorises forming a colourless liquid ethylene dibromide.

$CH_2 = CH_2 + Br_2 \rightarrow CH_2Br-CH_2Br$ (ethylene dibromide).

$CH_2 = CH_2 + HBr \rightarrow CH_3-CH_2Br$ (ethyl bromide).

The radical $CH_3 - CH_2 -$ or C_2H_5- is known as *ethyl.*

(b) hydrogen in presence of reduced nickel catalyst at 150°C :

$CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3$ (ethane).

(c) hypochlorous acid, HOCl :

$CH_2 = CH_2 + HOCl \rightarrow CH_2OH-CH_2Cl$ (ethylene chlorohydrin).

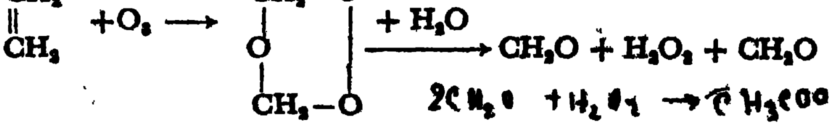
(d) concentrated sulphuric acid slowly in the cold but rapidly at 160°C :

$CH_2 = CH_2 + H.HSO_4 \rightarrow CH_3-CH_2.HSO_4$ (ethyl hydrogen sulphate)

The ethyl hydrogen sulphate gives ethyl alcohol on boiling with water.

$$CH_3.CH_2.HSO_4 + H.OH = C_2H_5OH + H_2SO_4$$

(e) Ozone, giving the unstable explosive substance ethylene ozonide which on hydrolysis yields formaldehyde, CH_2O, and hydrogen peroxide. The reaction is useful in detecting double bond in ethylene.



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + O_3 \longrightarrow \begin{matrix} CH_2-O \\ |\quad\quad | \\ O\quad\quad | \\ |\quad\quad | \\ CH_2-O \end{matrix} \xrightarrow{+H_2O} CH_2O + H_2O_2 + CH_2O$$

$2CH_2O + H_2O_2 \rightarrow 2HCOOH$

(v) **Oxidation reactions.**—Mild oxidising agents, such as cold dilute alkaline $KMnO_4$ solution, oxidise ethylene to glycol.

$CH_2 = CH_2 + H_2O + O \longrightarrow \underline{CH_2OH-CH_2OH}$ (ethylene glycol).

Absorbents.—(i) Bromine ; (ii) Concentrated sulphuric acid—fuming H_2SO_4 rapidly absorbs ethylene.

Test for unsaturation.—The presence of unsaturation in a hydrocarbon is readily detected by its decolorisation of bromine water or of cold dilute alkaline potassium permanganate solution (**Baeyer's test**).

Uses.—(i) In the preparation of mustard gas, and in the artificial ripening of fruits like apples, bananas and oranges, and as an anæsthetic.

(ii) In the preparation of ethylene dibromide for 'ethyl petrol' containing lead tetraethyl ; in the manufacture of ethyl alcohol ; in making the synthetic plastics *polythene* and *teflon*.

Acetylene, $H-C\equiv C-H$

History, *etc.*—Acetylene was discovered by Edmund Davy in 1836 but was carefully studied by Berthelot (1855) who synthesised the gas from its elements by striking an electric arc between two carbon electrodes in an atmosphere of hydrogen (fig. 134). It is highly endothermic.

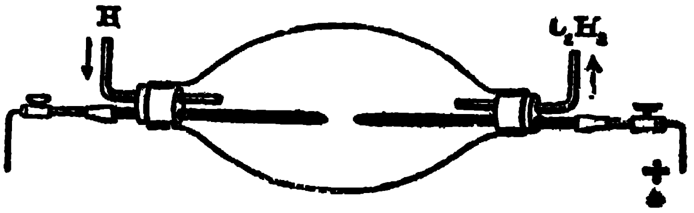


Fig. 134.

$$2C + H_2 \leftrightharpoons C_2H_2 - 54{,}860 \text{ cals.}$$

It is found to the extent of 0.6 per cent in coal gas. It is formed when a Bunsen burner 'strikes back'.

Laboratory preparation.—Acetylene is prepared in the laboratory, also commercially, by the action of cold water upon calcium carbide.

$$CaC_2 \text{ (calcium carbide)} + 2H_2O = Ca(OH)_2 + C_2H_2.$$

A small heap of calcium carbide is placed on a layer of sand covering the bottom of a conical flask. The air from the flask is first displaced by coal gas, and then water is allowed to drop slowly from a tap-funnel upon the calcium carbide. Acetylene is reaidly evolved, and is collected over water (fig. 60). $4Ca(OCl)Cl + PH_3 = 4CaCl_2 + H_3$

The acetylene from commercial calcium carbide has an unpleasant smell due to presence of hydrogen sulphide and phosphine usually. The crude gas is purified by passing through : (a) acid copper sulphate solution which absorbs the H_2S, and then (b) bleaching powder solution whereby the phosphine is oxidised and retained as phosphoric acid.

Pure acetylene is best obtained : (i) by passing the crude acetylene gas in ammoniacal cuprous chloride solution which absorbs acetylene, giving a red precipitate of cuprous acetylide, Cu_2C_2, and then decomposing the cuprous acetylide by heating with strong HCl or potassium cyanide solution. The gas may be dried over P_2O_5 and collected over mercury.

$$C_2H_2 + 2CuCl = Cu_2C_2 \text{ (cuprous acetylide)} + 2HCl$$

$$Cu_2C_2 + 2HCl = 2CuCl + C_2H_2$$

$$Cu_2C_2 + 2KCN + 2H_2O = 2CuCN + 2KOH + C_2H_2$$

(ii) by dropping ethylene bromide into boiling alcoholic potash, when pure C_2H_2 evolves. Monobromoethylene or vinyl bromide, $CH_2 = CHBr$, is formed in intermediate stage.

$$CH_2Br-CH_2Br + KOH \longrightarrow CH_2 = CHBr + KBr + H_2O$$

$$CH_2 = CHBr + KOH \longrightarrow CH \equiv CH + KBr + H_2O$$

Properties.—(i) A colourless gas with a sweet ethereal smell when pure (the unpleasant smell of the gas is due to the presence of impurties such as phosphine), acetylene is slightly lighter than air, and sparingly soluble in water—the gas is soluble in its own volume of water and *very soluble in acetone.*

(ii) Non-supporter of combustion, the gas burns with a smoky flame, separating much carbon and yielding water and carbon dioxide :

$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O.$$

A mixture of acetylene and air explodes with violence when ignited. On account of its highly endothermic charcater, compressed acetylene is likely to detonate, and therefore the gas is stored in solution (under pressure) in acetone absorbed in a porous material—acetone dissolves 300 vols. of the gas under 12 atmospheres.

(iii) **Action of chlorine.**—Acetylene explodes violently if mixed with chlorine, depositing soot : $C_2H_2 + Cl_2 = 2C + 2HCl$.

When small pieces of calcium carbide are dropped into a saturated solution of chlorine in a jar, there appear flashes of light with simultaneous separation of soot.

But by the regulated action of chlorine on acetylene in presence of a mixture of sulphur chloride and reduced iron, acetylene dichloride, CHCl = CHCl, and acetylene tetrachloride (*westron*), $CHCl_2.CHCl_2$, are produced—they are used as solvents.

$$C_2H_2 + Cl_2 = C_2H_2Cl_2 \; ; \quad C_2H_2 + 2Cl_2 = C_2H_2Cl_4.$$

The acetylene tetrachloride gives trichloroethylene, $CHCl = CCl_2$, (*westrosol*) on heating with lime.

$$2CHCl_2-CHCl_2 + CaO \longrightarrow 2CHCl = CCl_2 + CaCl_2 + H_2O.$$

This reaction is typical of many reactions of the doubly-unsaturated compound acetylene (containing a triple bond between the carbon atoms) in which 4 univalent atoms or groups are added to a molecule of acetylene to yield an additive compound. The action with chlorine may be represented as :

$$\begin{array}{c} CH \\ ||| \\ CH \end{array} + Cl_2 = \begin{array}{c} CHCl \\ || \\ CHCl \end{array} \qquad \begin{array}{c} CHCl \\ || \\ CHCl \end{array} + Cl_2 \quad \begin{array}{c} CHCl_2, \\ | \\ CHCl_2. \end{array}$$

(iv) **Addition reactions.**—Acetylene combines additively with :

(a) halogens, halogen hydracids, and strong sulphuric acid, etc.

$CH \equiv CH + 2Br_2 \rightarrow CHBr_2-CHBr_2.$

$CH \equiv CH + HBr \rightarrow CH_2 = CHBr$ (vinyl bromide).

$CH_2 = CHBr + HBr \rightarrow CH_3-CHBr_2$ (ethylidene bromide)

(b) hydrogen in contact with platinum black or finely divided nickel to ethylene and then ethane,

$$CH \equiv CH + H_2 \rightarrow CH_2 = CH_2 \text{ (ethylene)}$$

$$CH_2 = CH_2 + H_2 \rightarrow CH_3-CH_3 \text{ (ethane)}.$$

Ethylene is made technically by partial hydrogenation of acetylene in presence of palladium at 270°C.

(c) Acetylene is converted by **hydration** into acetaldehyde by passing into a hot dilute sulphuric acid at 60°C, containing mercuric sulphate which acts as a catalyst :

$$CH \equiv CH + H_2O \rightarrow CH_3-CHO \text{ (acetaldehyde)}.$$

The acetaldehyde is converted to *ethylalcohol* CH_3CH_2OH *by* reduction by hydrogen in presence of nickel at 100—140°C and to *acetic acid,* CH_3COOH, by oxidation by air in presence of manganous acetate. These reactions are important technically.

$$CH_3-CHO+H_2 = CH_3CH_2OH \; ; \quad CH_3-CHO + O = CH_3-COOH$$

(v) **Acetylides.**—Acetylene readily gives a *red precipitate of* cuprous acetylide with ammoniacal cuprous chloride solution and a *white* precipitate of silver acetylide with ammoniacal silver nitrate solution. These reactions provide a **sensitive test** for acetylene.

$$C_2H_2+2CuCl = C_2Cu_2+2HCl \; ; \quad C_2H_2+2AgNO_3 = C_2Ag_2+2HNO_3$$

Sodium acetylides C_2HNa and C_2Na_2 are formed by passing acetylene over heated sodium or a solution of sodium in liquid ammonia. Sodium acetylides are used to prepare alkyl derivatives of acetylene. Thus, sodium acetylide reacts with methyl iodide, CH_3I, in liquid ammonia solution to give methyl acetylene $CH_3.C \equiv CH$.

$$2\underline{CH \equiv CH + 2Na \longrightarrow 2CH \equiv C.Na + H_2} \quad H_2 \text{ from } CH \equiv CH$$

$$CH \equiv CNa + ICH_3 \longrightarrow CH \equiv C.CH_3 + NaI.$$

(vi) When *heated to dull redness,* acetylene undergoes polymerisation, yielding benzene : $3C_2H_2 = C_6H_6$.

Acetylene is a highly unsaturated compound and is also very unstable. The greater unstability and higher reactivity of acetylene compared to ethylene (which contains a *double bond*) is due to the presence of a *triple bond* in the molecule.

Absorbent.—Ammoniacal cuprous chloride, bromine, fuming sulphuric acid and acetone are used as absorbent for acetylene.

Uses.—(a) As an illuminant, and for generating oxy-acetylene flame for welding and cutting steel ; (ii) For the manufacture of acetaldehyde, ethyl alcohol and acetic acid ; (iii) In making synthetic rubber and plastics, (iv) Chlorinated acetylene, such as *westron,* $C_2H_2Cl_4$, and *westrosol,* C_2HCl_3, are non-inflammable liquids and are used as solvents for fats, oils and resins.

***Cyanogen,** $(CN)_2$, is evolved by heating mercuric cyanide to dull redness in a hard glass tube. The gas may be collected over mercury.

Cyanogen is a highly *poisonous,* colourless gas, soluble in water. With water it forms hydrocyanic and cyanic acid (cf. chlorine).

$$Hg(CN)_2 = Hg + (CN)_2 \; ; \quad (CN)_2 + H_2O = HCN + HCNO.$$

It is absorbed by alkali, forming cyanide and cyanate.

$$(CN)_2 + 2NaOH = NaCN + NaCNO + H_2O.$$

***Hydrocyanic acid,** HCN, is prepared by distilling potassium cyanide with a mixture of equal volume of sulphuric acid and water—the vapour of HCN is evolved. This is dried by calcium chloride and liquefied in a tube cooled in freezing mixture :

$$KCN + H_2SO_4 = KHSO_4 + HCN$$

Anhydrous hydrocyanic acid is a colourless gas, b.p. 25.65°. It burns with a purple flame in air :

$$4HCN + 5O_2 = 2H_2O + 2N_2 + 4CO_2.$$

It is a dangerous poison (0.06—0.07 g. is fatal). It is a very weak acid, weaker than even the carbonic acid. It is used in fumigation for killing insects.

A solution of HCN is obtained by distilling potassium ferrocyanide with *dilute* sulphuric acid (1 : 2). A highly diluted solution is used as a remedy for bronchial catarrh. Diluted to 2.6 p.c. HCN it is called *prussic acid.*

Comparison of CH_4, C_2H_4 and C_2H_2

Properties	CH_4	C_2H_4	C_2H_2
1. Nature, colour, smell, etc.	Colourless, odour less gas.	Colourless gas with a sweet-smell.	Colourless gas with a sweet smell, if pure.
2. Density	Lighter than air; density 8(H = 1)	Nearly as heavy as air; density 14(H = 1).	Slightly lighter than air; density 13(H = 1)
3. Solubility in water	Sparingly soluble; 5.56 vols. in 100 vols. at 0°C; 3.3 vols. at 20°C.	Slightly soluble; 0.163 vol. in 1 vol. at 13°C.	1 vol. in 1 vol. at 15°; *Very soluble in acetone.*
4. Combustibility, etc.	Non-supporter of combustion; burns with a feebly luminous flame.	Non-supporter of combustion; burns with a luminous flame.	Non-supporter of combustion; burns with a sooty flame.
5. When mixed with air or O_2 and fired.	Explodes violently; 1 vol. requires 2 vols. of O_2.	Explodes violently; 1 vol. requires 3 vols. of O_2.	Detonates explosively; 1 vol. requires 2.5 vols. of O_2.
6. Action of H_2.	No action, since CH_4 is a *saturated hydrocarbon.*	An *unsaturated* hydrocarbon with a *double bond* reacts additively with 2 atoms of H_2 in presence of Ni-catalyst: $C_2H_4 + H_2 = C_2H_6$.	An *unsaturated* hydrocarbon with a *triple bond* reacts additively with 4 atoms of H_2 in presence of Ni-catalyst: $C_2H_2 + 2H_2 = C_2H_6$.
7. Action of Chlorine.	(*i*) Explodes in direct sunlight, forming HCl and C. $CH_4+2Cl_2 = C+4HCl$. (*ii*) Forms substitution products CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 in diffused sunlight, since CH_4 is a saturated hydrocarbon.	(*i*) Burns when ignited, forming HCl and C. $C_2H_4+2Cl_2 = 2C+4HCl$. (*ii*) Reacts additively with 2 atoms of Cl_2. $C_2H_4+Cl_2 = C_2H_4Cl_2$, since C_2H_4 is unsaturated and contains a double bond.	(*i*) Bursts into flame, forming HCl and C. $C_2H_2+Cl_2 = 2C+2HCl$. (*ii*) Reacts additively with 4 atoms of Cl_2 in presence of sulphur chloride: $C_2H_2+2Cl_2 = C_2H_2Cl_4$. since C_2H_2 is unsaturated and contains a triple bond.
8. Action of halogen acids, HBr HI, etc.	No action	Adds 1 molecule. $C_2H_4 + HBr = C_2H_5Br$	Adds 2 molecules. $C_2H_2 + 2HBr = C_2H_4Br_2$
9. Bromine water or cold dilute alkaline $KMnO_4$.	No action	Decolorises, hence unsaturated.	Decolorises, hence unsaturated.
10. Ammoniacal Cu_2 Cl_2 solution.	No action	No action	Red precipitate of Cu_2C_2.
11. Absorbent.	—	Bromine and fuming H_2SO_4.	Bromine and fuming H_2SO_4; also ammonical Cu_2Cl_2 solution.

Separation of CH_4, C_2H_4 and C_2H_2

The gas mixture is passed through ammonical cuprous chloride solution when C_2H_2 alone is absorbed, forming red precipitate of Cu_2C_2.

Red precipitate of Cu_2C_2 is boiled with KCN solution—pure C_2H_2 is given off.

The mixture of residual gases CH_4 and C_2H_4 is passed through fuming H_2SO_4, when C_2H_4 alone is absorbed forming ethyl hydrogen sulphate.

The liquid containing ethyl hydrogen sulphate gives off C_2H_4 on heating.

The unabsorbed gas is CH_4.

The composition of gaseous hydrocarbons.—The composition of gaseous hydrocarbons such as methane, ethylene, and acetylene, etc., is found by explosion with an excess of oxygen in a eudiometer. A certain volume of a pure hydrocarbon is collected over mercury in the closed limb of a U-shaped eudiometer—the level of mercury is then brought to the same height in both limbs and the volume read off. A measured excess of oxygen is then introduced into the closed limb and the volume of the mixture is then read after levelling the mercury. The open limb is then closed with the thumb and an electric spark is sent through the gas mixture—water and carbon dioxide are formed on explosion. The water condenses to liquid on cooling, occupying negligible volume. The eudiometer is cooled after sparking, the level of mercury is again adjusted, and the volume of carbon dioxide formed and the excess of oxygen left unused is noted—*there always occurs a contraction on explosion.*

A piece of solid caustic potash is then introduced into the closed limb when the carbon dioxide is absorbed. The volume of the residual gas which is the unused oxygen is finally noted.

Let the volume of hydrocarbon = m c.c.
volume of oxygen = n c.c.
volume after sparking = p c.c.
volume after KOH absorption = q c.c.
∴ volume of CO_2 formed = (p-q) c.c. = x c.c.
and volume of O_2 used up = (n-q) c.c. = y c.c.

Now, vol. of O_2 used up in oxidising the carbon = vol. of CO_2 formed = x c.c.

∴ vol. of O_2 used up in the combustion of hydrogen = $(y-x)$ c.c., which corresponds to a volume of 2 $(y-x)$ c.c. of hydrogen in the free state.

The results actually observed are shown in a table :*

Gas	Vol. taken in c.c.	Vol. of CO_2 formed in c.c.	Vol. of O_2 used up in c.c.	Vol. of O_2 combining with H_2 in c.c.	Vol. of H_2 in c.c.
Methane	m	m	2 m	m	2 m
Ethylene	m	2 m	3 m	m	2 m
Acetylene	m	2 m	2.5 m	0.5 m	m

The formulæ of the hydrocarbons.—The results of explosion show that :

(*a*) 1 c.c. of methane gives 1 c.c. of CO_2 and contains H_2 equivalent to 2 c.c. in the free state.

∴ 1 mole of methane gives 1 mole of CO_2 and contains 2 moles of hydrogen. *By Avogadro's hypothesis.*

or 1 mole of methane contains 1 atom of carbon and 4 atoms of hydrogen. since 1 mole of CO_2 contains 1 atom of carbon and hydrogen is diatomic.

∴ the formula of methane is CH_4, which is confirmed by its vapour density of 8.

(*b*) 1 c.c. of ethylene gives 2 c.c. of CO_2, and contains H_2 equivalent to 2 c.c. in the free state.

∴ 1 mole of ethylene gives 2 moles of CO_2 and contains 2 moles of hydrogen.

or 1 mole of ethylene contains 2 atoms of carbon and 4 atoms of hydrogen, since 1 mole of CO_2 contains 1 atom of carbon and hydrogen is diatomic.

∴ formula of ethylene is C_2H_4, which is confirmed by its vapour density of 14.

(*c*) 1 c.c. of acetylene gives 2 c.c. of CO_2 and contains H_2 equivalent to 1 c.c. in the free state.

∴ 1 mole of acetylene gives 2 moles of CO_2 and contains 1 mole of hydrogen. since 1 mole of CO_2 contains 1 atom of carbon and hydrogen is diatomic.

∴ formula of acetylene is C_2H_2, which is confirmed by its vapour density of 13.

Fuel.—A fuel is a combustible substance which evolves heat on ignition with the oxygen of the air. It may be solid, liquid, or gaseous, and always contains carbon and usually hydrogen also. The chief raw fuel are coal and mineral oil (petroleum). Coal may be used directly as a fuel, or it may be converted into : (a) coal gas and coke by dry distillation, or (b) gaseous fuels such as producer gas, etc., or (c) liquid fuels by hydrogenation.

The destructive distillation of coal is known as **carbonisation of coal.** Coal may be carbonised at high (about 1000—1200°) or low temperature (about 600—650°C). In either case the main products are *coal gas*, *coal tar* and *coke*, but the products of the two processes differ in quality.

Coal gas of the low temperature process has higher calorific value. Low temperature tar yields motor spirit and fuel oils on distillation, while that of the other process contains benzene, toluene, naphthalene, carbolic acid etc. Low temperature coke is *soft* ; it burns without *smoke* but more freely than the high temperature coke. The high temperature coke, on the other hand, is *hard* and is suitable in metallurgy ; it burns with smoke.

The *calorific value* of a fuel is measured by the number of British thermal units (B. Th. U.) evolved by the complete combustion of 1 lb. of a solid or 1 cu. ft. of a gaseous fuel. The calorific value of bituminous coal is about 14,950 B. Th. U. per lb. and that of coal gas is about 560 B. Th. U. per cu. ft. of the gas. 1 B. Th. U. is the amount of heat required to raise the temperature of 1 lb. of water through 1°F.

Coal gas.—Coal gas is the gaseous product, mainly a mixture of combustible gases, produced by the carbonisation (destructive or dry distillation) of coal. Its approximate average composition in percentage by volume is :

(i) *Non-illuminating but heat-producing*	: hydrogen ...	45—50
	methane ...	30—50
	carbon monoxide ...	5—10
(ii) *Illuminants (unsaturated hydrocarbons)*	: ethylene, acetylene and benzene ...	2.5—5
(iii) *Diluents (inerts)*	: Nitrogen ...	2—10
	Carbon dioxide ...	0—2
	Oxygen ...	0—1
(iv) *Impurities*	: hydrogen sulphide, etc., if any,	

Besides the coal gas, other products (i.e. by-products) of distillation of coal are tar, ammoniacal liquor, coke and gas carbon.

Coal gas was first obtained by Rev. John Clayton in 1688 by the destructive distillation of coal but it was first introduced as an illuminant by William Murdock in 1792.

In gas-works practice only bituminous coal is carbonised. Powdered bituminous coal is distilled in a row of horizontal fire clay retorts, externally heated by the combustion of producer gas in a furnace (fig. 135)—the temperature being 1000° to 1200°C. The volatile products given off are led by vertical iron ascension pipes from the retorts into a long horizontal tube, called *hydraulic main*, which acts as a water-seal, preventing any gas escaping when the retort doors are opened for recharging. In the hydraulic main partial separation into crude gas, tar and ammoniacal liquor occurs. Much tar and ammoniacal liquor separate and is deposited in the hydraulic main where the temperature is about 60° only. The gas leaving the main contains traces of H_2S, NH_3, HCN, and CS_2 as impurities. The gas next passes through :

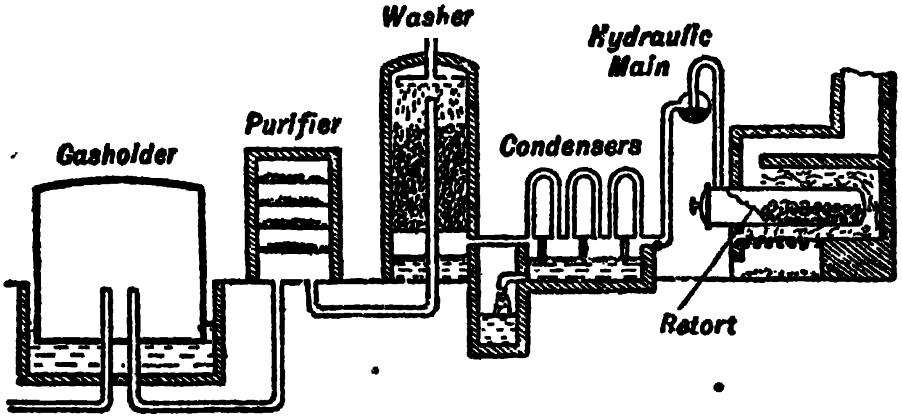


Fig. 135

(i) a series of air or water-cooled iron pipes, called *condensers*, where it is cooled to atmospheric temperature and hence more tar and ammoniacal liquor separate and collect in the tar well in two layers—the top layer being ammonical liquor and the bottom layer tar :

(ii) a rotary *suction pump* (*exhauster*) which drives the gas forward through the subsequent purifiers into the gas holder. From the exhauster the gas passes to :

(iii) *a tar separator* in which any accompanying tar fog separates and deposits as droplets. The gas then passes through :

(iv) an iron tower (called a *scrubber*) which is packed with coke, and down which a stream of water trickles—all traces of tar and ammonia are washed away with water in the scrubber. The scrubbed gas still contains H_2S and CS_2 as impurities, and passes to :

(v) the *purifier* which are iron boxes containing hydrated ferric oxide spread on shelves. Ferric oxide reacts with the hydrogen sulphide, forming ferric sulphide :

$$2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 6H_2O.$$

The oxide is revived by exposure to moist air, when sulphur is separated and hydrated ferric oxide is regenerated, to be used over again : $2Fe_2S_3 + 6H_2O + 3O_2 = 4Fe(OH)_3 + 6S$.

When the iron oxide contains about 50% free sulphur, it is used as a source for sulphur for making sulphuric acid, and is then known as *spent oxide of iron.* Purification of coal gas thus offers a method of recovery of sulphur from coal.

Carbon disulphide, CS_2, is then removed by passing the gas over heated nickel at 430° when it is converted into hydrogen sulphide which is removed as usual by moist ferric oxide :

$$CS_2 + 2H_2 = C + 2H_2S.$$

Sometimes H_2S is absorbed by slaked lime, when carbon disulphide is also simultaneously removed as calcium thiocarbonate.

$$Ca(OH)_2 + 2H_2S = Ca(SH)_2 + 2H_2O \; ; \quad Ca(SH)_2 + CS_2 = CaCS_3 + H_2S.$$

The hydrogen sulphide liberated is absorbed in a second lime purifier.

The sulphur content of coal gas is carefully regulated—the purified gas must contain less than 1 part of H_2S in 10 millions.

Hydrocyanic acid HCN is removed either as *ferrocyanide* by passing the gas through a purifier containing an alkali and ferrous sulphate :

$$FeSO_4 + 6HCN + 6NaOH = Na_4Fe(CN)_6 + Na_2SO_4 + 6H_2O,$$

or as *ammonium thiocyanate* by passing the gas through ammoniacal liquor containing ammonia, ammonium sulphide, and sulphur in suspension.

$$(NH_4)_2S_2 + NH_4OH + HCN = (NH_4)_2S + NH_4CNS + H_2O.$$

The purified gas is finally stored in gas-holder, which are iron tanks floating on iron or masonry trough, containing water, by the aid of weights suspended by pulleys.

The weight of coal gas obtained is about 17% of the weight of coal carbonised, i.e., about 380 lbs. per ton of coal. The tar, ammoniacal liquors and coke form 5%, 8% and 70% respectively, of the weight of coal.

Coal gas burns with a smoky flame, forming CO_2 and H_2O. It is a colourless gas with a peculiar smell and possesses reducing properties. Its calorific value is about 560 B. Th. U. per cubic foot.

Coal gas finds extensive use as an illuminant in cities and towns—Welsbach mantle which contains thoria and 1 or 2 per cent ceria, is heated to incandescence in gas light. It is also used as a fuel. Electricity is gradually becoming serious rival to coal gas, since the use of the former ensures better control of temperature and cleaner operation. Coal gas, however, maintains its position because of its important by-products. Coal gas also finds use in metallurgy.

Carbonisation is now generally carried out in vertical retorts which admit of a continuous operation—coal is fed continuously to the top and the coke continuously drawn from the bottom of the retort. Coal is often carbonised in coke-ovens, particularly when hard coke for metallurgy is required. Coke oven gas is more or less similar to coal gas in composition.

By-products of the coal gas industry.—(i) **Coal tar** : On fractional distillation it gives benzene, toluene, naphthalene, carbolic acid, creosote oil, etc. which are the starting materials for obtaining numerous dyes, drugs, perfumes and explosives. The coal tar pitch is used for road making. Coal tar directly or the creosote oil is used for preserving timber, water-proofing gunny bags, etc.

(ii) **Ammoniacal liquor** : On boiling with milk of lime it yields ammonia which is usually fixed by sulphuric acid as *ammonium sulphate* to be used as a fertiliser.

(iii) **Coke :** This is a residue left in the retort after the distillation of coal and is extensively used as a domestic fuel and in metallurgy.

(iv) **Gas carbon :** It is obtained as a hard dense deposit inside the retort due to the thermal decomposition of gaseous hydrocarbons in contact with the hot walls of the retort. A good conductor of heat and electricity, it is used in making electrodes.

(v) **Spent iron oxide :** It contains sulphur and cyanogen compounds and is used for the preparation of potassium ferrocyanide and for the recovery of sulphur. **Gas lime** (or **spent lime**) from the purifier is used as a manure.

Crude benzene is nowadays extracted from coal gas by washing with a suitable oil, and is recovered ; the naphthalene vapour present in the coal gas (which tends to deposit as a solid in the pipes) is also taken out by this process.

Fuels produced by the gasification of coke.—(*a*) **Producer gas** (also called air gas), is obtained by passing a limited supply of air through a bed of *white-hot* (temperature 1000°C) coke—the reaction is *exothermic*. The gas is made in closed cylindrical steel furnaces lined with fire-bricks, called producers (fig. 136) in which a large mass of hot coke rests on a grating G, through which the air is admitted. The coke is stoked through P, and E is the exit for the producer gas. The reactions in the formation of producer gas are :

$$2C + O_2 = 2CO + 58{,}000 \text{ cals.} \qquad \text{(i)}$$

$$C + O_2 = CO_2 + 97{,}000 \text{ cals.} \qquad \text{(ii)}$$

$$CO_2 + C \rightleftharpoons 2CO - 39{,}000 \text{ cals.} \qquad \text{(iii)}$$

Any CO_2 formed is reduced to CO by the heated coke ; the reduction is endothermic and hence the temperature of the bed of coke is kept high at about 1000°C. The ratio of CO/CO_2 increase with increase in temperature. The producer gas is mainly CO and N_2 ; its average composition in percentage is : H_2 10, CH_4 2, CO 20, CO_2 4, N_2 64.

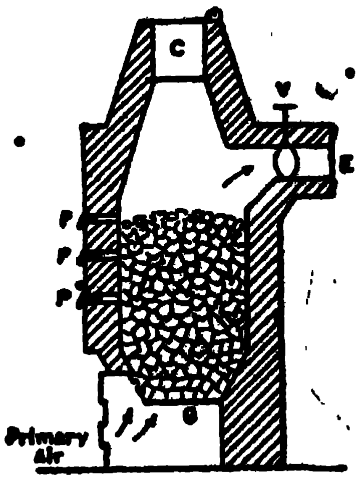


Fig. 139

Its calorific value is about 150 B. Th. U. per cu. ft. It is used as a fuel in heating coal-gas retorts and in furnaces and gas engines.

(*b*) **Water gas** is obtained by blowing steam through a bed of *white-hot* (temperature 1000°C) coke—it is chiefly a mixture of equal volumes of carbon monoxide and hydrogen. The reaction is highly *endothermic*. Reactions are :

$$C + H_2O \rightleftharpoons CO + H_2 - 39{,}000 \text{ cals. (bright red heat)} \qquad \text{(i)}$$

$$C + 2H_2O \rightleftharpoons CO_2 + 2H_2 - 29{,}000 \text{ cals. (dull red heat)} \qquad \text{(ii)}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O - 10{,}000 \text{ cals.} \qquad \text{(iii)}$$

The CO_2 is converted into CO at high temperatures by the water gas reaction—the proportion of CO increases with temperature :

Temp. °C	% steam decomposed	H_2	CO	CO_2
840	41	61.9	15.1	22.9
1010	94	48.8	49.7	1.5
1125	99.4	50.9	48.5	0.6

Steam is blown through a bed of incandescent coke in a producer but as the water gas reaction absorbs heat and the coke-bed gradually cools, the proportion of CO_2 in the gas goes on increasing. The supply of steam is, therefore, cut off after a time (8 minutes), and air is blown in through the coke for a short period (2 minutes) until the necessary high temperature to begin the *endothermic water gas* reaction is regained, the air gas formed being turned to waste. So the blowing of steam and air alternates, The water gas invariably contains some carbon dioxide. Its average composition is : H_2 48, CH_4 1, CO 42, CO_2 3, N_2 6.

Its calorific value is about 300 B. Th. U. per cu. ft. It is added to coal gas to make town gas, and is also used as a source for hydrogen, and as a reducing agent in metallurgy. Water gas is also called *blue water gas,* as it burns with a pale blue flame.

(*c*) **Semi-water gas** is obtained by passing a mixture of air and steam continuously through a bed of red-hot coke—the amount of steam mixed with air is so adjusted that the endothermic water gas reaction is just balanced by the exothermic producer gas reaction, and hence the temperature of the coke is kept constant. The semi-water gas is usually known as *producer gas.* Its average composition in percentage by volume is :

$$H_2\ 12,\ CH_4\ 3,\ CO\ 30,\ CO_2\ 2,\ N_2\ 53.$$

Its calorific value is about 180 B. Th. U. per cu. ft. It is used as a fuel and as a source for nitrogen and hydrogen for the manufacture of synthetic ammonia.

Mond gas is made with a mixture of air and a large excess of steam which keep the temperature low (650°) and allows the recovery of nitrogen of coal as ammonia.

Carburetted water gas.—Water gas alone burns with a blue non-luminous flame but may be used as an illuminant with Welsbach mantle. It can be used as an illuminant by *carburetting* it, i.e., mixing with hydrocarbons, partly unsaturated, which burn with a luminous flame.

In making carburetted water gas two towers packed with chequer-brick, called *carburettor* and *superheater*, are placed after the water gas generator. During the 'blow' period (2 minutes) air is blown through hot bed of coke in the generator, which is thereby heated to incandescence, and the producer gas formed is mixed with air and burnt in the carburettor and the superheater to heat the chequer-bricks. During the 'make' period (4 minutes) steam is blown through the heated coke, and the water gas is passed through the hot carburettor down which is injected a spray of mineral oil which vaporises. The mixture of water gas and oil vapour then passes through the red-hot bricks in the superheater, where the oil vapour is *cracked*, i.e., decomposed into gaseous hydrocarbons rich in ethylene. The gas is freed from tar and then sent through a purifier in which H_2S is removed by hydrated ferric oxide, and finally stored in gas holders (fig. 137).

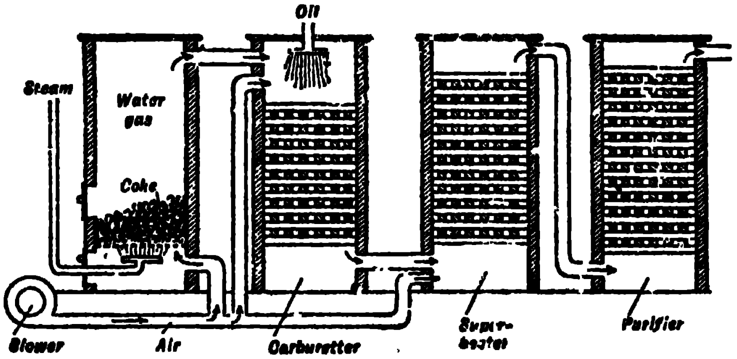


Fig. 137

Oil Gas.—The oil gas is commonly used in many chemical laboratories in India. It is usually prepared by cracking kerosene oil—a thin continous stream of the oil is allowed to flow into a cast-iron retort (fig. 138) heated to redness by coal-fire. The liquid hydrocarbons, of which the oil is made, crack, i.e., decompose into simpler gaseous hydrocarbons methane, ethane, ethylene, etc. The gas is first passed through a scrubbing box in which the tarry matter is deposited, and then collected over water in gas holders.

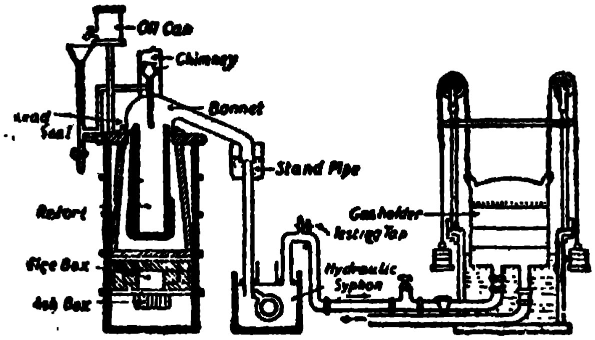


Fig. 138

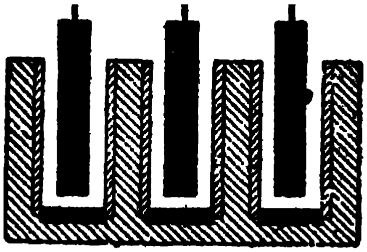


Fig. 139

Calcium carbide, CaC_2, is manufactured by heating a mixture of 3 parts of quick lime and 2 parts of coke at a temperature of about 2500—3000°C in an electric furnace. Lime must not contain magnesium oxide. The coke is the hard coke, free from dust and of low ash content. A carbide furnace is a steel box divided into compartments lined with firebrick and then an inner lining of gas carbon—a graphite block being stamped in the base to form an electrode. The other electrode consists of a bundle of carbon rods which is lowered into the furnace (fig. 139). The furnace is partly an arc and partly a resistance furnace. The reaction is $CaO+3C = CaC_2+CO$. Molten carbide is drawn off, solidified and crushed to pieces.

Hard, dark grey solid, it reacts with cold water, yielding acetylene :

$$CaC_2 + 2HOH = C_2H_2 + Ca(OH)_2.$$

At about 1100° it absorbs nitrogen yielding a mixture of calcium cyanamide and graphite. It is used as a fertiliser under the name nitrolim.

$$CaC_2 + N_2 = NaCaN + C.$$

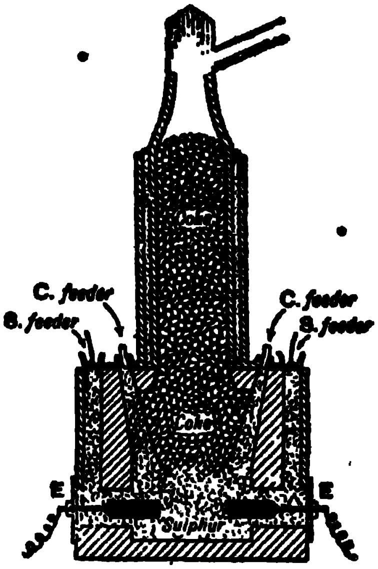


Fig. 140

Carbon disulphide, CS_2, is obtained by the action of sulphur vapour upon white-hot coke in a furnace (fig. 140) fitted at the base with carbon electrodes to set up an electric arc. Sulphur is run under the electrodes and coke introduced above the electrodes. At the temperature of the arc sulphur volatalises and reacts with carbon, yielding carbon disulphide which passes through a column of charcoal to remove any unchanged sulphur vapour. The carbon disulphide vapour condenses to a colourless liquid of b.p. 46°C. It is highly inflammable and poisonous. It dissolves sulphur, phosphorus and iodine. It burns in air or nitric oxide :

$$2CS_2+5O_2 = 2CO+4SO_2 \, ; \, 2CS_2+10NO = 2CO+4SO_2+5N_2.$$

Carbon disulphide is used to make viscose rayon (artifical silk) and in the vulcanisation of rubber. Sodium xanthate, made by heating CS_2 with alcoholic caustic soda, is used for ore floatation.

It reacts with chlorine, yielding carbon tetrachloride—a reaction of commercial importance : $CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2$. A non-inflammable liquid, carbon tetrachloride is used as a solvent, and as a fire extinguisher under the name *pyrene*. *It should, however, not be sprayed on sodium fire,* as it reacts explosively with hot sodium.

Combustion.—Substances such as coal, oil, etc., burn in air or oxygen with evolution of much heat and light—the burning of a substance in air or oxygen is ordinarily called combustion. The process is one of oxidation, since burning involves combination with oxygen. But in a more general sense :

Combustion means any chemical reaction attended with evolution of heat and light.

Substances like arsenic, antimony, phosphorus, etc., for example, catch fire with flashes of light in chlorine ; this is as good an instance of combustion as of coal gas or hydrogen burning in air. Combustion may, therefore, take place even in absence of oxygen. Now, since oxidation involves combination with any electro-negative element such as oxygen, chlorine, etc. *combustion is a phenomenon of oxidation in a general sense.*

Slow combustion.—Many substances, such as moist iron, undergo slow oxidation, when exposed to air, without catching fire, since the heat produced dissipates too rapidly to raise the mass to the ignition point—moist iron is converted into rust by what is called the process of *slow combustion.* Respiration is but slow combustion.

Explosion.—Explosion is an extremely *rapid combustion,* heat, light and also sound following in its wake. The rate of the chemical reaction is very fast in explosion. The velocity of a chemical reaction is slower at lower temperatures, and consequently if the heat of combusion is rapidly lost by radiation or conduction, the inflammable mixture does not get sufficiently heated to burn fast enough to cause explosion. But if the temperature of the inflammable mixture is gradually raised, a temperature, known as *the ignition temperature,* is finally reached when the rate of the reaction is so fast that the heat liberated by the reaction exceeds the heat lost to such as extent that an *instantaneous combustion* or what is called *explosion* occurs.

Surface combustion—When a combustible mixture such as coal gas and air is injected through the pores of granular firebricks placed near or around the objects to be heated, the brick gets intensely heated and a huge quanity of heat is concentrated at its surface, which radiates the heat to the object. This phenomenon of *flameless surface combustion* is of practical consequence as the transmission of heat to the object is extremely rapid.

Incandescence.—Incandescence is a phenomenon which is attended with the emission of light, usually observed at high temperatures. It may or may not be accompanied by combustion. The incandescent light obtained by the combustion of magnesium involves a chemical reaction, viz., $2Mg + O_2 = 2MgO$, whereas the limelight, i.e., the white incandescent light emitted from the surface of lime when the oxy-hydrogen or oxy-acetylene flame is impinged on it, is not attended with combustion, i.e., without any chemical change. The gas mantle is simply heated to incandescence to emit light.

The phlogiston theory of combustion (page 6) was discarded as a result of the classical researches of Lavoisier.

Reciprocal combustion.—In combustion coal gas, hydrogen etc., burn in an atmosphere of air—coal gas, hydrogen, etc., are said to be *combustible* and the envelope of air *supporter of combustion.* But the combustion would also take place equally well if the coal gas or hydrogen be the enveloping medium, since it is the chemical reaction between coal gas or hydrogen and air that is taking place. The functions of the substances that are combustible and supporter of combustion are, therefore, interchangeable, and the terms combustible and supporter of combustion are relative and are determined by experimental conditions.

Experiment.—A glass chimney (fig. 141) is fitted with a cork at the bottom through which pass two tubes, and covered with an asbestos sheet with a hole in its centre. The chimney is filled with coal gas which is passed through the shorter of the tubes. Coal gas, escaping at the top of the chimney, is ignited when a gas-flame in an envelope of air is produced. Air is passed through the longer tube and ignited by pushing the tube up to the burning coal gas and is then pushed down to the middle of the chimney when an air flame in an envelope of coal gas is obtained. Hence the terms '*combustible*' and '*supporter of combustion*' are relative. It is known as *reciprocal combustion.*

The experiment may be carried out with any pair of gases which show the phenomenon of combustion, e.g., hydrogen and oxygen; methane and oxygen.

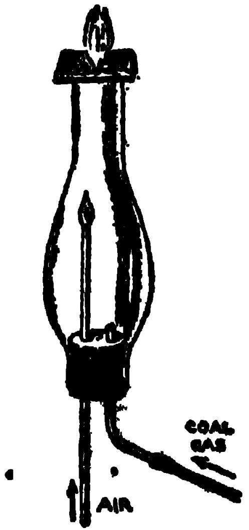


Fig. 141

Ignition point.—For every combustible substance there is a temperature which must be reached before it takes fire in air—this temperature is known as the ignition point. A substance, such as phosphorus, whose ignition point is below the atmospheric temperature *spontaneously* catches fire in air. Phosphorus dihydride, P_2H_4, is also spontaneously inflammable.

During his investigations on the causes and prevention of explosions in coal mines, occasioned by the ignition of mixtures of methane and air (*fire damp*) when naked flames were used, Davy in 1815 carried out the following experiments on the ignition of combustible gases :

When a wire gauze of fine mesh is pressed over a Bunsen flame, the flame does not pass through the gauze, owing to the cooling effect produced by the conduction of heat by the metal ; but on holding the gauze for some time, the temperature of the metal reaches the ignition point, when the gas ignites and burns above the gauze.

Similarly, when a wire gauze is held over an unlighted gas burner, the gas passing through may be ignited above the gauze, but the flame does not pass through and ignite the gas below the gauze.

The ignition point of methane was found to be high, so that it was not kindled by red-hot metal.

These experiments led Davy to the invention of *safety lamp* bearing his name. It is essentially an oil lamp (fig. 142) enclosed in a cylinder of fine wire gauze. When such a lamp is taken in coal mines where the fire damp exists, the latter passes into the lamp inside the gauze and burns there. But the flame is not propagated to the gas outside, since the heat is rapidly conducted away by the metal gauze. Hence the inflammable atmosphere outside never reaches the ignition point.

The *flash point* of a liquid fuel, such as kerosene oil, is the temperature at which it gives out a vapour which is ignited by a flame.

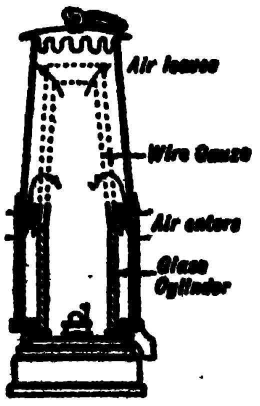


Fig. 142

Flame.—When a combustible gas or vapour burns, the hot glowing atmosphere immediately above it may be described as the flame. It may be defined as *a zone in which chemical reaction between gases takes place with evolution of heat and light.* Much energy is liberated in chemical reactions producing a flame, and the emission of light is caused by the chemical reactions.

The flame may either be *luminous* or *non-luminous.* Ethylene, acetylene, coal gas and candle flames are all luminous. The alcohol and the Bunsen flames are non-luminous. Hydrogen burns with a pale blue but hardly visible flame.

Chemiluminescence may be regarded as a cold flame, i.e., light without heat. Phosphorescence, i.e., the glow of phosphorus in the dark is a familiar example. When ether is dropped on a hot iron plate so that it is not kindled, a greenish phosphorescent flame is noticed in the dark.

Combustible liquids such as paraffin, and solids such as wax, sulphur and phosphorus, can burn with a flame only when they are first converted into their vapours. An incandescent mass of coke, on the other hand, burns without a flame.

The structure of flame.—The structure of flame depends upon the nature of the gas. A *hydrogen* or *carbon monoxide flame* burning in air or oxygen, consists of two zones, an inner cone of unburnt gas and an outer cone where the combustion takes place.

$$2H_2 + O_2 = 2H_2O \; ; \; 2CO + O_2 = 2CO_2.$$

The *ammonia flame* in oxygen has three cones, an inner one of unburnt gas surrounded by a yellow cone where decomposition of ammonia takes place, $2NH_3 \leftrightharpoons N_2 + 3H_2$, and an outer pale greenish yellow cone in which hydrogen burns. The structure of a flame of *hydrogen sulphide* or *carbon disulphide* vapour in air or oxygen is similar.

Candle flame.—A candle flame (fig. 143) consist of four zones—(a) **The dark inner cone of unburnt gas or vapour of wax** ; *this is the zone of no combustion.*

A match head quckly thrust inside this zone, does not ignite for some time. On inserting one end of a bent glass tube inside the inner zone, the unburnt gas passes out of the tube and may be ignited at the upper end. These experiments show that the flames are hollow.

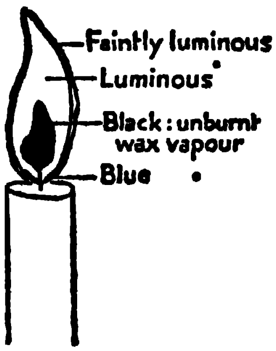


Fig. 143

(b) **A brightly luminous zone of partial combustion,** occupying most of the flame. The luminosity is due to incandescent carbon particles. Soot deposits on the outer surface when a clean porcelain basin is held on the luminous flame. *It is the reducing flame.*

Hydrocarbons are thermally decomposed at this zone into free carbon particles and acetylene and other dense hydrocarbons which are but incompletely oxidised here.

(c) **A bright blue region** at the base of the flame where combustion takes place without separation of carbon ;

At the blue zone at the base the hydrocarbon is partially oxidised to CO which causes the characteristic colour on burning :

$$CH_4 + O_2 = CO + H_2 + H_2O$$

(d) **A faintly luminous mantle,** surrounding the flame completely. This is the zone of complete combustion, as there is free access of air at this region, and hence the hottest region. *It is the oxidising zone.*

The candle flame is a typical **hydrocarbon flame.** The **luminous coal gas flame,** i.e., the Bunsen flame with air hole closed is similar to the candle flame.

Faraday's experiment.—The structure of a candle flame is shown by the following experiment of Faraday. The short end of a glass siphon is lowered into the flame and the long end inside a flask (fig. 144) :

(i) With the tube in the inner cone of unburnt vapour, i.e., just above the wick, white vapours of wax pass over into the flask ; (ii) on raising the tube into the bright luminous zone, dense black vapours containing carbon particles, pass over ; (iii) on raising the tube further in the outer mantle, water drops collect in the flask, and also carbon dioxide as is shown by adding lime water which turns milky.

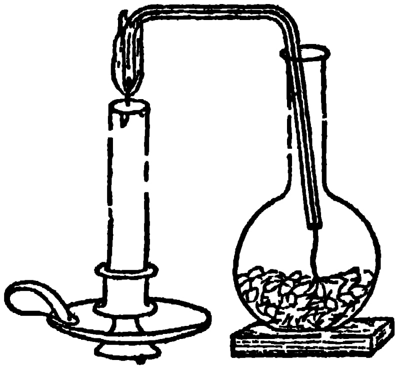


Fig. 144

The luminosity of flame.—One or the other or often two or three together of the following causes, are responsible for the luminosity. They are :

(a) **Presence of incandescent solid matter in the flame :** According to Davy (1816) the luminosity of a hydrocarbon flame is due to the incandescent solid carbon particles produced in the flame by the thermal decomposition of combustible gas. The presence of solid carbon particles in luminous hydrocarbon flames is a fact to support Davy's theory.

Flames containing solid particles, such as those of Mg, Zn, and K in oxygen are highly luminous.

A non-luminous flame is made luminous by introducing solid particles into it. Clouds of smoke from burning camphor, for example, when admitted through one of the air holes of a Bunsen burner by means of a funnel tube render the flame luminous.

Coal gas flame is made luminous by inserting a gas mantle in it. Oxy-hydrogen flame, when directed against a block of lime, produces intensely white light.

But Davy's theory alone is not sufficient to explain luminosity in all cases. Phosphorous, phosphine, H_2S, and CS_2, etc., for example, burn with a luminous flame which are unlikely to contain any solid particles at the high temperatures attained.

(b) **The presence of dense gas in the flame :** Frankland observed in 1861 that the luminosity of a candle flame on the top of a mountain is much feebler than in a valley. He further noticed that a candle or coal gas flame in a partly exhausted bell-jar is much less luminous than in free air. Consequently, *the denser a gas, the greater* the *luminosity of its flame.* Luminosity is, therefore, increased by compression.

Hydrogen burns in oxygen under a pressure of 20 atmospheres, giving a luminous flame. An alcohol flame burning in air at 4 atmospheres becomes luminous.

The luminosity of coal gas flame, according to Frankland, is due to the glow of incandescent *dense gaseous hydrocarbons* like naphthalene and benzene vapours.

But the presence of solid carbon particles have been proved in luminous hydrocarbon flames. Frankland's theory may apply to flames where no solid particles are present.

According to Lewis the luminosity of a hydrocarbon flame is due to the intermediate formation of acetylene—heat of decomposition of endothermic acetylene adds to the temperature of the flame. Carbon is separated as fine particles. $2CH_4 = C_2H_2 + 3H_2 = 2C + 4H_2$.

(c) **The temperature also affects the luminosity of flame :** The higher the temperature, the greater is the luminosity. This explains the luminosity of the flame of carbon disulphide or phosphine—no solid particles separating during their combustion.

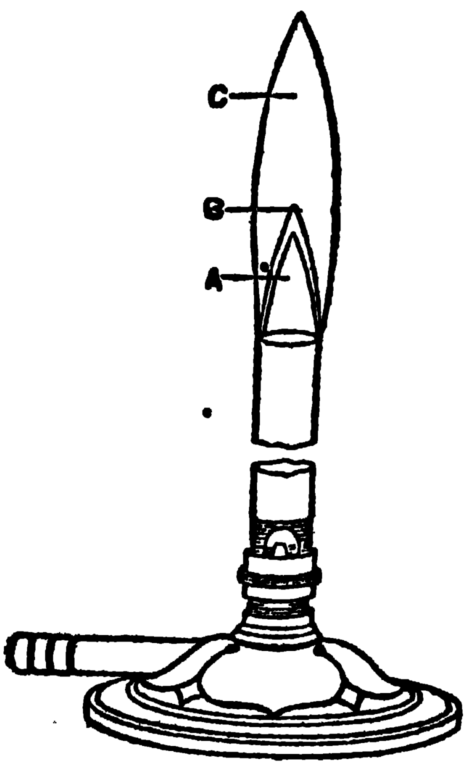


Fig. 145

The Bunsen burner.—The Bunsen burner (fig. 145) is a device for burning coal gas—the coal gas being mixed with sufficient air *before* combustion. It consists of a *base* with a side tube ending in a *jet*, over which is screwed a metal tube, called *burner tube*, with a hole (*air hole*) opposite the jet—round the tube is slipped a short metal ring, called *air regulator*, with a hole corresponding to that in the tube.

The side tube is connected by a rubber tubing with the main gas supply—the stream of coal gas passing out of the jet causes a reduction of pressure, and *with the air hole open*, air is sucked in through it into the burner tube and mixes with the gas. The mixture of gas and air burns on ignition at the top of the tube, giving a *non-luminous flame*.

The Bunsen flame.—(i) *With the air holes closed*, the coal gas burns at the top with flickering **luminous flame** and resembles the structure of a candle flame and consists of *four zones*, *vide supra*.

(ii) *With the air holes open*, sufficient air is drawn in through the burner tube and gets mixed with the gas—the combustion is therefore complete without any free carbon particles remaining in the flame to render it luminous. The flame from the combustion of such a mixture differs from the former in as much as the outer zone of complete combustion increases in thickness, the luminous region gradually disappears and the flame becomes shorter and steady, and an inner cone of pale blue colour is seen and the coal gas-air mixture burns with a **non-luminous flame** with **two cones** :

(a) a pale blue inner cone of gas with incipient combustion—*it is the reducing zone* : The inner cone becomes green and shrinks when a large volume of air is admitted. (b) a still paler blue outer cone of complete combustion—*it is the oxidising zone*. The outer cone remains constant in size. The tip of the outer cone is the hottest part of the flame. Incomplete oxidation of the hydrocarbon gases occur in the inner cone with the formation of reducing gases CO and H_2, which burn completely in excess of air in the outer cone.

The more the air that is sucked in, the hotter the flame. But the inner cone becomes *green* and the flame begins to 'roar' when a large quantity of air is admitted. With too much of air or too less of the gas, the flame *strikes back*, from the mouth of the burner, i.e., runs down the tube, and the gas begins to burn at the mouth of the jet. Acetylene is formed when the burner 'strikes back' and the gas burns at the jet, and the burner tube becomes extremely hot.

The flame is prevented from striking down by keeping the upward speed of the gas-air stream equal to the speed of the propagation of the flame downwards. When a flame strikes back, this is avoided either by decreasing the air-supply by regulating the air-holes or by increasing the gas supply. But the best course is to turn off the gas, as the air-gas mixture becomes dangerously explosive.

Non-luminosity of the Bunsen Flame.—Three factors, *viz.*, *oxidation*, *dilution*, and *cooling*, play a part to make the Bunsen flame non-luminous :

(*i*) *Oxidation* :—All the carbon is burnt without previous deposition, there being therefore, no free carbon particles in the flame to add to its luminosity.

(*ii*) *Dilution* :—When the air-coal gas mixture is diluted before combustion with inert gases such as CO_2, N_2 and steam, the flame is rendered non-luminous, higher temperature being required for the separation of carbon from the diluted coal gas.

(*iii*) *Cooling* :—A hydrocarbon flame becomes non-luminous on being cooled, on bringing a cold piece of iron plate in contact with a luminous flame of coal gas burning at a fish-tail burner, the flame loses its luminosity but no soot is deposited. Cooling and dilution hinder the separation of carbon prior to the gases reach the outer zone where complete combustion occurs in excess of oxygen.

The Bunsen burner was devised by Robert Bunsen in 1855 and is commonly used in the laboratory. Teclu and Meker burners are also in use when a very hot flame is required.

The **temperature of flames** in degrees Centigrade are as follows :

Bunsen-coal-gas flame	1871°	Oxy-coalgas blow-pipe	2200°
Acetylene-air ,,	2548°	Oxy-acetylene ,,	3200°
Hydrogen-air ,,	1900°	Oxy-hydrogen ,,	2420°
Methane-air ,,	1670°	Electric arc ,,	3760°
Caron monoxide-air ,,	1700°	Sun ,,	7800°

White heat 1200°. Dull red heat 500°C. Bright red heat 800°C.

Exercises

1. What is meant by allotropy ? Give an account of the different allotropic forms of carbon. How would you establish that diamond is nothing but carbon ?

How would you show that all the allotropes of carbon are one and the same element ? *Nagpur '30*

2. Describe one method in each case by which (a) carbon monoxide, (b) carbon dioxide can be prepared in the laboratory. Under what conditions do these gases react with caustic soda ? How would you analyse quantitatively a mixture of carbon monoxide, carbon dioxide and nitrogen ?

3. Describe how the composition of carbon dioxide has been determined by weight and by volume. What function does the gas play in the growth of plants ? *Calcutta Inter.*

4. Explain the reactions that take place when (a) calcium carbonate is heated with coke, (b) carbon dioxide is passed into lime water, (c) the solid product that separates on continued passing of carbon dioxide, into caustic soda solution, is heated, (d) carbon dioxide is passed over red hot charcoal, (e) ignited magnesium inserted in a jar of carbon dioxide, (f) carbon monoxide is passed over finely divided nickel, (g) carbon monoxide is passed over heated iron oxide. How would you prove that a carbonate contains carbon ?

5. How is methane usually prepared and purified in the laboratory ? What happens when it is (a) led over red hot copper oxide, (b) burnt in an atmosphere of chlorine ? How would you prove that 2 volumes of steam and 1 volume of carbon dioxide can be obtained from 1 volume of methane ? *Madras Inter.*

How could you distinguish between hydrogen and methane ?

6. What is meant by the term hydrocarbon ? Compare the properties of methane, ethylene and acetylene. How are they detected in a mixture, and separated from each other ? Deduce a general method of finding their composition. *Calcutta '59*

7. How is acetylene prepared and purified in the laboratory ? Explain what happens when it is (a) led into a jar of chlorine, (b) passed into hot mercuric sulphate in dilute sulphuric acid, (c) ammoniacal cuprous chloride solution, (d) passed through a red hot tube. *Calcutta '59*

8. How would you remove small quantities of (a) carbon dioxide from ethylene, (b) carbon dioxide from carbon monoxide, (c) acetylene from ethylene ? Discuss the reactions of chlorine with methane and ethylene. How would you establish that a carbonate contains carbon ?

9. Describe the changes which take place when (a) air, (b) steam is passed over heated coke, and explain the bearing of the changes on the method used, for the manufacture of water-gas. How is hydrogen obtained from water-gas ? *Bombay Inter.*

10. What is coal gas ? Describe the preparation and purification of the gas. What are the by-products of coal gas manufacture ? *Calcutta '53*

11. Explain clearly what is meant by the terms combustion and oxidation. Show by means of suitable experiments that the terms combustible and supporter of combustion are only relative. What is meant by slow combustion ? *Punjab '49*

12. What is a flame ? Explain fully the structure of a candle flame. Is there any difference between a candle flame and that of a Bunsen burner ? If so, explain the nature and cause of the difference. What are the cause of luminosity of a flame ? *Nagpur '39*

13. What is meant by ignition point ? Describe Davy's experiments on the ignition of gases. What is the cause of explosions in coal mines and how can it be prevented ?

14. How would you distinguish between two gas-jars that contain : (a) nitrogen and carbon dioxide, (b) hydrogen and carbon monoxide, (c) carbon monoxide and carbon dioxide, (d) ethylene and acetylene, (e) methane and carbon monoxide. How would you analyse quantitatively a sample of gas containing ethylene, acetylene and methane ?

15. Explain what is meant by carbonisation of coal. Describe in outline the manufacture of coal gas. What are the main constituents of coal gas ? What is the structure of the coal gas flame when the gas is burnt in a Bunsen burner : (i) with air hole open, (ii) with air hole closed ?

How would you determine the amounts of hydrogen, methane and carbon monoxide in a sample of coal gas ?

16. How would you convert (a) carbon monoxide into carbon dioxide, (b) carbon dioxide into monoxide ? Calculate the weight of carbon dioxide that can be obtained by heating 21 gm. of sodium bicarbonate. *Ans.* 5.5. gm.

How would you obtain a sample of solid sodium bicarbonate ?

17. What reactions take place when air is passed through a tube containing : (a) a long layer of red-hot coke, (b) a short-length of red-hot coke ? What are the products when (a) carbon dioxide, (b) steam, are passed separately through a bed of charcoal heated to bright redness ?

18. Explain how you would distinguish : (a) fully burnt limestone from a partially burnt sample ;

(b) crystalline sodium carbonate from a sample of sodium bicarbonate ;

(c) carbon dioxide from carbon monoxide. How would you detect traces of carbon monoxide in foul air ?

19. Describe manufacture of oil-gas in your college laboratory.

XXIV

Phosphorus

Formula P_4 ; Atomic weight 30.98 ; Atomic number 15 ; B. Pt. 280.5° ; M. Pt. 44.1° ; Density 1.83 yellow, 2.20 red.

Discovery.—In 1674-5 Brand, an alchemist of Humburg, who was seeking philosopher's stone, accidently discovered phosphorus by distilling evaporated urine —the phosphate, $Na(NH_4)\ HPO_4$, in the urine on heating forms the metaphosphate, $NaPO_3$, which is reduced to phosphorus by carbon separated from the charred organic matter.

$$4NaPO_3 + 5C = Na_4P_2O_7 + 5CO + 2P.$$

The element was called phosphorus, since it glows in the dark (*Phos = light ; phero =* I bear). In 1777 Scheele made phosphorus by distilling phosphoric acid with charcoal.

Occurrence.—Phosphorus occurs always in the combined state and mainly as phosphates. The chief minerals are : **fluorapatite,** $3Ca_3(PO_4)_2,CaF_2$, and **chlorapatite,** $3Ca_3(PO_4)_2$, $CaCl_2$—they are *hard* phosphates and are insoluble in dilute acids. Other phosphate minerals are **sombrerite** and **phosphorite,** $Ca_3(PO_4)_2$, *vivianite,* $Fe_3(PO_4)_2$, $8H_2O$, and **wavelite,** $4AlPO_4$, $2Al(OH)_3$, $9H_2O$. **Coprolites** (calcium phosphate from fossil excreta) is a *soft-phosphate* and is soluble in dilute sulphuric acid.

As a nomal constitutent of plant and animal tissues, it is essential to their growth. It occurs especially in seeds, the yolk of eggs, the nerves and brain, and bone marrow, usually in the form of *lecithins* or glycero-phosphates. It is an essential constituent of bones in the form of calcium phosphate. Bones contain about 58 p.c. calcium phosphate plus some calcium carbonate, fat and nitrogeneous organic matter. The fat may be extracted with carbon tetrachloride, and the organic matter dissolved out with hot water under pressure as *glue* or *gelatin,* and the residue then charred in closed retorts to form *animal charcoal* which is used in decolorising sugar. When no longer active, this is burnt to yield a residue called **bone ash,** containing about 80 per cent calcium phosphate, with a little calcium carbonate and fluoride. *Bone ash is an important source of phosphorus.*

The preparation of phosphorus—

(i) In the old process bone ash or soft mineral phosphate was decomposed by hot and fairly strong (60 per cent) sulphuric acid, yielding phosphoric acid and insoluble calcium sulphate which was filtered off.

$$Ca_3(PO_4)_2+3H_2SO_4 = 3CaSO_4+2H_3PO_4.$$

The filtrate was concentrated to a syrup mixed with charcoal and dried until the phosphoric acid was converted to meta-phosphoric acid, HPO_3. The dried mass was distilled in fire clay retorts (fig. 146) at bright-red heat—the vapour of phosphorus passing over was condensed under water.

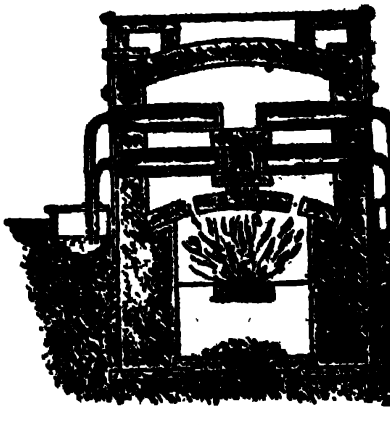


Fig. 146

$$H_3PO_4 = HPO_3+H_2O\ ;$$

$$4HPO_3+12C = P_4+2H_2+12CO.$$

This process has been superseded by the electric furnace method.

(ii) **The electric furnace method.**—Phosphorus is now made by heating a phosphate mineral with sand and coke at a high temperature in an electric furnace by the *Readman, Parker and Robinson process*. A mixture of bone ash or mineral phosphate such as *apatite, sand and coke* is introduced through a hopper into a *closed electric furnace* made of brick work (fig. 147)—the charge being carried into the furnace by a screw conveyer. An electric arc is struck between carbon electrodes set towards the bottom of the furnace, to heat the charge. At the high temperature of the furnace, at about 1150°, silica displaces the more strongly acidic phosphorus pentoxide, owing to the volatility of the latter, forming calcium silicate. Phosphorus pentoxide is then reduced by the coke at about 1500°, to phosphorus vapour and carbon monoxide which leave the furnace by an exit at the top and bubbles through *water* under which phosphorus vapour condenses to yield *white phosphorus* and CO passes out. Fusible calcium silicate is run off at the bottom as a slag.

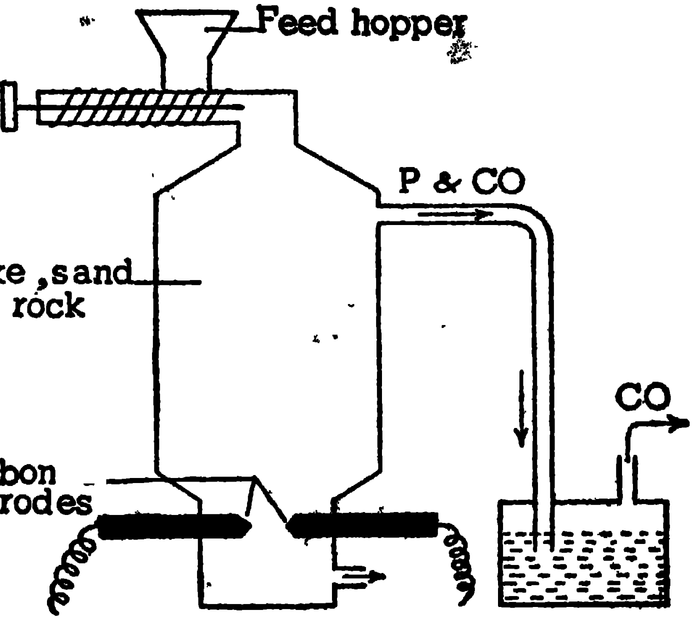


Fig. 147

$$Ca_3(PO_4)_2+3SiO_2=3CaSiO_3+P_2O_5\ ;\qquad 2P_2O_5+10C=P_4+10CO.$$

Crude phosphorus thus obtained is melted under hot water to separate it from sand, and stirred with a mixture of potassium dichromate and strong sulphuric acid ; some impurities are oxidised and pass into solution, and others separate and rise as a scum ; the liquid is filtered by pressing through chamois leather, cast into sticks by running into glass tubes cooled in water and finally packed with water in tin cans. *White phosphorus is stored and transported under water as it inflames in air.*

Properties of phosphorus.—(i) White (or yellow) phosphorus is a translucent, soft, waxy, white, crystalline, low-melting solid, very sparingly soluble in water (1 in 300,000) but, *readily soluble in carbon disulphide*, ether, olive oil, benzene and alcohol. It is a non-conductor of heat and electricity. *It is higly poisonous*—the lethal dose being about 0.15 gm. Its vapour density corresponds with P_4.

(ii) It ignites in air at the low temperature of 35°, yielding phosphorus pentoxide, and hence *phosphorus is always kept and handled under water.* $4P + 5O_2 = 2P_2O_5$.

Exposed to air at the ordinary temperature white phosphorus undergoes spontaneous oxidation, yielding white fumes of a lower oxide and some ozone and emitting a *green glow* or **phosphorescence**, visible in the dark.

Even a trace of phosphorus (1 in 500,000) gives this glow and its formation is used to detect phosphorus in cases of phosphorus poisoning.

Expt. *1.*—On carefully adding concentrated sulphuric acid to a mixture of pieces of white phosphorus and potassium chlorate kept under water in a jar, phosphorus ignites under water, giving sparks of fire under water.

Expt. *2.*—Small pieces of phosphorus are placed in a test tube half-filled with water—the tube is supported in a beaker of hot water. On gently heating the water in the beaker to 60° and slowly passing oxygen through the tube the phosphorus melts, takes fire and burns under water.

Expt. *3.*—A solution of phosphorus in carbon disulphide is poured on a piece of blotting paper; the carbon disulphide rapidly evaporates, and the phosphorus inflames, yielding white fumes of phosphorus pentoxide.

Expt. *4.*—**Cold flame experiment.**—Few pieces of dry white phosphorus are placed in a flask and covered with dry glass wool—the flask is fitted with a cork and two tubes. The flask is heated on a water-bath and a stream of carbon dioxide is passed through. The phosphorus vapour carried along with the gas oxidises in the air and a *green flame* of glowing phosphorus is produced at the mouth of the exit tube. The flame is quite cold to the hand and does not kindle a match.

The phosphorescent light of fireflies is due to the oxidation of a substance known as *luciferin* by the enzyme *luciferase.*

(iii) It inflames spontaneously in halogens, yielding halides of phosphorus :

$$P_4+6Cl_2 = 4PCl_3\ ;\quad P_4+10Cl_2 = 4PCl_5\ ;\quad P_4+6I_2 = 4PI_3.$$

(iv) It dissolves in hot caustic alkali, yielding phosphine and hypophosphite : $P_4+3NaOH+3H_2O = PH_3+3NaH_2PO_2$.

(v) It is oxidised to phosphoric acid by hot concentrated nitric acid. $P_4+10HNO_3+H_2O = 4H_3PO_4+5NO+5NO_2$.

White phosphorus must never be touched with fingers. It is cut *under water* with a knife using tongs.

(vi) White phosphorus reacts with cold copper sulphate, giving metallic copper ; white phosphorus, if accidentally dropped on the hand, may be removed by washing with copper sulphate solution :

$$2P + 5CuSO_4 + 8H_2O = 5Cu + 2H_3PO_4 + 5H_2SO_4.$$

Colloidal solution of gold is obtained by reducing auric chloride solution with phosphorus dissolved in ether.

Phosphorus liberates iodine from acidified potassium iodate solution.

$$2P + 2KIO_3 + H_2SO_4 + 2H_2O = 2H_3PO_4 + K_2SO_4 + I_2.$$

In cases of phosphorus poisoning copper sulphate is administered as an emetic, followed by hydrogen peroxide.

Allotropy of phosphorus.—Two main allotropes of phosphorus are : (a) *white* (or *yellow*) *phosphorus,* (b) *red phosphorus.* White phosphorus, is metastable at the ordinary temperature and is slowly transformed into the stable red variety with evolution of heat.

$$P(\text{white}) = P(\text{red}) + 4{,}220 \text{ calories.}$$

Red phosphorus.- phosphorus is obtained by subjecting white phosphorus to si *electric discharges* or by heating it at 250° in an atmosphere of nit or carbon dioxide in presence of a trace of iodine as a catalyst.

Red phosphorus is obtained by heating white phosphorus in a cast iron pot (fig. 148) fitted with an air-tight cover through which passes an upright tube, open at both ends, so that the pressure inside the pot does not exceed one atmosphere. The temperature is kept at 240°. A portion of phosphorus is oxidised by the oxygen of air in the pot, and the rest is slowly transformed into solid red phosphorus. The red phosphorus thus obtained is cooled, ground under water, boiled w caustic soda solution to remove any unchanged white phosphorus, and filtered. It is then washed with hot water and dried with steam.

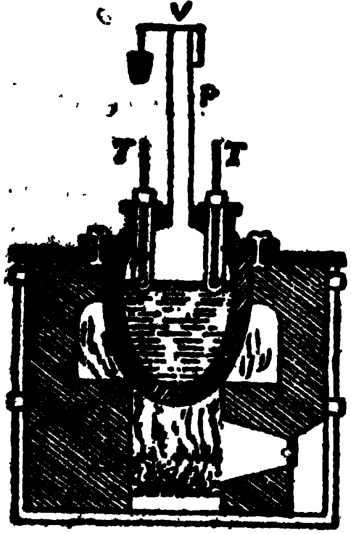


Fig. 148

On heating, the red phosphorus is directly converted into vapour, which condenses to white phosphorus on cooling.

Experiment.—Conversion of red phosphorus to yellow : A little red phosphorus is placed in a hard glass test tube, fitted with a rubber stopper and two tubes. The air within the test tube is displaced by a current of carbon dioxide. The red phosphorus is then heated in a slow current of carbon dioxide when white phosphorus condenses on the upper cooler part of the test tube.

Besides the red phosphorus, other stable forms of phosphorus are : (i) **scarlet phosphorus,** amorphous, prepared by boiling a solution of white phosphorus in phosphorus tribromide for several hours, (ii) **violet phosphorus,** crystalline, and non-conductor of electricity, prepared by crystallising white phosphorus from molten lead, and (iii) **black phosphorus,** crystalline and *fairly good conductor of electricity,* prepared by heating white phosphorus at 200° under 12,000 atmospheres. All the forms are insoluble in CS_2.

Ordinary red phosphorus is a mixture of scarlet and violet phosphorus. Reddish violet crystalline solid without any smell and taste, *non-poisonous,* insoluble in water, ether, carbon disulphide and caustic alkalis, red phosphorus is quite stable at the ordinary temperature, and does not spontaneously inflame in air. It burns in chlorine when heated. Commercial red phosphorus is a feeble conductor of electricity.

Comparison of white and red phosphorus.—White phosphorus is unstable ; it slowly passes into red phosphorus which is stable. White phosphorus is however more reactive chemically than red phosphorus. They differ greatly in their physical and chemical properties :

Property	White phosphorus	Red phosphorus
1. Colour	Colourless or pale yellow	Reddish-violet
2. Smell	Garlic smell	Odourless
3. Specific gravity	1.83	2.20
4. Melting point	44.1°	592.5° under pressure
5. Boiling point	280.5°	Very high
6. Ignition temp. in air	35°C	260°C
7. Solubility in water	Very sparingly soluble	Insoluble
8. Solubility in CS_2	Soluble	Insoluble

9. Action of air	Spontaneous oxidation with green glow or phosphorescence	Does not glow, i.e., no phosphorescence ;
10. Action of chlorine	Ignites spontaneously	Ignites on heating.
11. Hot caustic alkali	Dissolves evolving PH_3	No action
12. Chemical activity	Ver reactive	Less active than white P
13. Electrical conductivity	Non-conductor	Feeble conductor
14. Stability	Metastable allotrope	Stable allotrope
15. Physiological action	Intensely poisonous	Non-poisonous.

Uses of Phosphorus.—(i) In the manufacture of matches—yellow phosphorus in lucifer matches, and red phosphorus in safety matches, (ii) In the preparation of phosphorus pentoxide, phosphor bronze, hypophosphite of lime, and red phosphorus, (iii) In making tracer bullets, incendiary bombs, and in producing smoke screen, and (v) As a poison for rats.

Hydrides of phosphorus.—Two well-defined hydrides of phosphorus are : gaseous *phosphorus trihydride* PH_3 (*phosphine* or *phosphoretted hydrogen*) and liquid *phosphorus dihydride* P_2H_4.

Phosphine.—Phosphine is prepared in an impure condition by heating *white phosphorus* with a strong solution of caustic alkalis. Pieces of white phosphorus and a 30 to 40 per cent solution of caustic soda are taken in a flask (fig. 149) fitted with an inlet tube dipping in the solution and a delivery tube, the free end of which dips under water in a trough. The air in the flask is displaced by a current of *coal-gas* sent through the inlet tube, and the flask is then gently heated, when phosphine evolves. As each bubble of the gas escapes out of water, it catches fire spontaneously with a bright flash, producing a vortex ring of white smoke (of phosphorus pentoxide) rising in the air. The reaction produces phosphine and sodium hypophosphite :

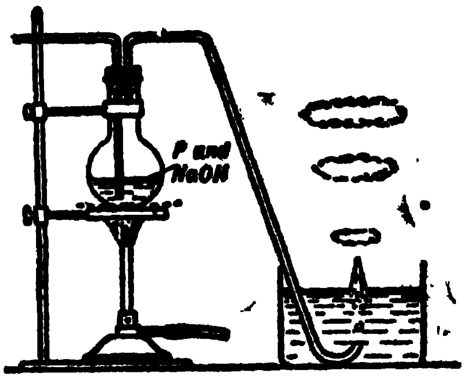


Fig. 149

$$P_4+3NaOH+3H_2O = PH_3+3NaH_2PO_2.$$

Pure phosphine is not spontaneously inflammable in air. The spontaneous inflammability of the gas thus prepared is due to the presence of the vapour of liquid hydrogen phosphide, P_2H_4. The principal impurities are hydrogen and P_2H_4, formed by the reactions :

$$6P+4NaOH+4H_2O = 4NaH_2PO_2+P_2H_4.$$

$$2P+2NaOH+2H_2O = 2NaH_2PO_2+H_2.$$

P_2H_4 may be removed as follows : The impure gas is passed through a U-tube, cooled in freezing mixture, when P_2H_4 condenses to a liquid, and phosphine is then collected over water, the phosphine thus collected is no longer spontaneously inflammable.

Properties.—(i) A colourless, poisonous, heavier-than-air gas with an unpleasant *smell of rotten fish*, phosphine is sparingly soluble in water—*the solution is neutral to litmus.* Its b. p. is −87.4° and m. p. −132.5°.

(ii) It burns readily in air, yielding phosphorus pentoxide and water ; impure phosphine is spontaneously inflammable.

(iii) It ignites spontaneously in chlorine, yielding phosphorus trichloride and hydrogen chloride. A mixture of phosphine and nitrous oxide explodes when sparked.

$$2PH_3+4O_2 = P_2O_5+3H_2O \; ; \quad PH_3+3Cl_2 = PCl_3+3HCl.$$

$$PH_3+4N_2O = H_3PO_4+4N_2.$$

(iv) It is *faintly basic* and forms unstable phosphonium salts with halogen acids. Caustic alkalis decompose phosphonium salts' liberating phosphine.

$$PH_3+HI = PH_4I \; ; \quad PH_4I+KOH = KI+H_2O+PH_3.$$

(iv) It is a *powerful reducing agent,* and precipitates mixtures of metal and phosphide from solutions of cupric and silver salts.

Besides the distinctive odour of decaying fish, phosphine may be *detected* by the formation of a black precipitate of cupric phosphide, when passed into an *acidified* solution of cupric sulphate.

$$3CuSO_4+2PH_3 = Cu_3P_2 + 3H_2SO_4.$$

When passed into silver nitrate solution, phosphine forms a black precipitate of metallic silver, a yellow intermediate compound being formed :

$$PH_3 + 6AgNO_3 = Ag_3P,\, 3AgNO_3 + 3HNO_3.$$

$$Ag_3P,\, 3AgNO_3 + 3H_2O = 6Ag + 3HNO_3 + H_3PO_3.$$

(vii) The gas is *absorbed* by a solution of bleaching powder.

(vii) **Composition of phosphine.**—It is decomposed into hydrogen and red phosphorus by heat to 400° or electric sparks. Its composition may be determined in this way. A known volume of pure and dry phosphine is collected over mercury in a eudiometer and sparked unitl there is no more increase in volume (fig. 95). Two volumes of phosphine yield three volumes of hydrogen ; hence the formula is PxH_3. But its molecular weight is 34, density being 17, as found experimentally.

$\therefore \; 31x + 3 = 34$ whence $x = 1$. Hence the formula is PH_3.

A gas which is not spontaneously inflammable but contains hydrogen as an impurity, may be obtained by heating phosphorus with alcoholic potash.

A spontaneously inflammable gas is formed by the action of water on calcium phosphide : $Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3$.

Pure phosphine.—Pure phosphine is prepared : (i) by the action of 30 per cent caustic potash solution on phosphonium iodide.

$$PH_4I + KOH = KI + H_2O + PH_3.$$

The evolved gas is washed with hydrochloric acid (to decompose P_2H_4) and caustic soda solution (to remove HI), and finally dried over phosphorus pentoxide, and then collected over mercury.

Phosphonium iodide is prepared directly by the action of water upon a mixture [illegible] iodine and white phosphorus. Phosphorus and iodine are dissolved in carbon disulphide in a retort from which air is displaced by carbon dioxide. The carbon disulphide is distilled off, and then on adding water to the phosphorus iodide and heating the retort, phosphonium iodide sublimes into a receiver attached to the end of the retort. $2P + I_2 + 4H_2O = H_3PO_4 + PH_4I + HI$.

(ii) by the reaction of dilute H_2SO_4 upon aluminium phosphide made by heating a mixture of aluminium powder and red phosphorus.

$$2AlP + 3H_2SO_4 = Al_2(SO_4)_3 + 2PH_3.$$

(iii) by heating phosphorous acid : $4H_3PO_3 = 3H_3PO_4 + PH_3$.

Comparison of phosphine and ammonia.—Phosphorus belongs to the same group in the periodic system as nitrogen, and forms a hydride phosphine, which is analogous to ammonia, as the following properties clearly illustrate.

Phosphine	*Ammonia*
1. A colourless, heavier-than-air gas with a *smell of rotten fish.*	1. A colourless, lighter-than-air gas with a *pungent smell.*
2. Sparingly soluble in water ; solution neutral to litums.	2. Highly soluble in water, solution alkaline turning red litmus blue.
3. Non-supporter of combustion, it ignites in air of oxygen. $2PH_3 + 4O_2 = P_2O_5 + 3H_2O$.	3. Non-supporter of combustion, it ignites in *excess air* or oxygen. $4NH_3 + 3O_2 = 2N_2 + 6H_2O$.
4. *Faintly basic ;* forms unstable phosphonium salts with halogen acids ; caustic alkali decomposes these salts, yielding phosphine.	4. *Highly basic ;* forms ammonium salts with halogen acids ; caustic alkali decomposes these salts, yielding ammonia.
5. Ignites spontaneously in chlorine, forming phosphorus trichloride and hydrogen chloride. $PH_3 + 3Cl_2 = PCl_3 + 3HCl$.	5. Reacts with excess of chlorine giving nitrogen trichloride and hydrogen chloride. $NH_3 + 3Cl_2 = NCl_3 + 3HCl$.
6. A powerful reducing agent, pricipitates copper, silver and gold from solution of their salts at ordinary temperature.	6. A reducing agent only at high temperature ; reduces heated cupric oxide or lead monoxide to the metallic state.
7. Precipitates metallic phosphides from solutions of silver and cupric salts.	7. Precipitates metallic hydroxides from solutions of many metallic salts ; e.g., $AlCl_3$, $FeCl_3$.
8. Decomposes into its elements by heating to 440° or by sparking.	8. Dissociates into its elements by strong heating or sparking.
9. Highly poisonous.	9. Non-poisonous.

Phosphorus dihydride, P_2H_4.—It may be prepared by the action of warm water upon calcium phosphide. It is spontaneously inflammable and has no basic properties. $Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + P_2H_4 + H_2$.

Halides of phosphorus—Phosphorus directly combines with halogens, yielding PX_3 or PX_5 according as the phosphorus or the halogen is in excess. These halides are completely hydrolysed by water to phosphorus and phosphoric acids respectively :

$$PX_3 + 3H_2O = H_3PO_3 + 3HX \; ; \quad PX_5 + 4H_2O = H_3PO_4 + 5HX.$$

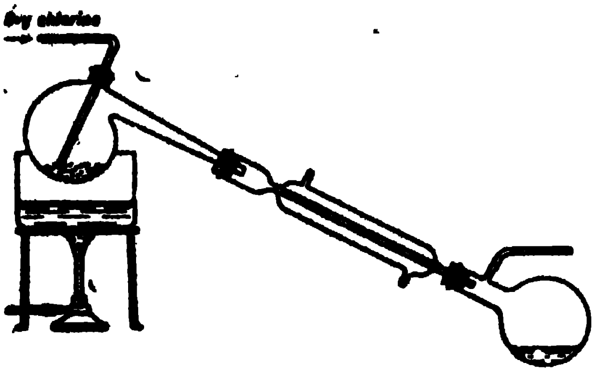


Fig. 150

The fluorides of phosphorus are gases, phosphorus trichloride and tribromide are liquids, the remaining halides of phosphorus are solids. *PI_5 does not exist.*

Phosphorus trichloride is prepared by passing *dry* chlorine over white phosphorus taken in a retort (fig. 150) which is gently heated on a water bath—the air in the retort being previously displaced by carbon dioxide. Phosphorus trichloride distils and collects in a well-cooled receiver. It is freed from any penta chloride or excess chlorine by redistillation with white phosphorus.

A colourless liquid, b. pt. 76°, it is hydrolysed by water, giving phosphorus acid and hydrogen chloride.

$$2P + 3Cl_2 = 2PCl_3\,; \qquad PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

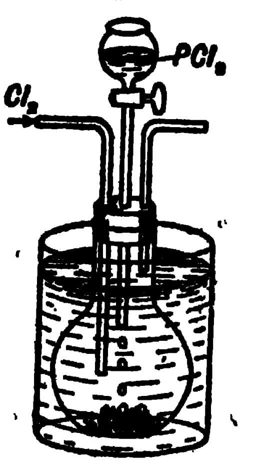


Fig. 151

Phosphorus pentachloride is obtained as a white powder by burning phosphorus in excess of chlorine or by passing chlorine into well-cooled phosphorus trichloride. A stream of dry chlorine is passed into a flask (fig. 151) cooled in ice, while phosphorus trichloride is slowly run into the flask from a tap-funnel. PCl_5 collects as a white powder in the flask. It dissociates by heat, giving phosphorus trichloride and chlorine. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. It is hydrolysed by water, giving phosphorus oxychloride, and finally phosphoric acid. $POCl_3$ is a fuming liquid, b. pt. 107.2°.

$$PCl_5 + H_2O = POCl_3 + 2HCl\,;$$
$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$

Oxides and oxyacids of phosphorus.—The principal oxides and oxyacids of phosphorus are :

Phosphorus trioxide, P_2O_3
Phosphorus tetroxide, P_2O_4
Phosphorus pentoxide, P_2O_5

Hypo-phosphorous acid, H_3PO_2
Phosphorous acid, H_3PO_3
Hypo-phosphoric acid, $H_4P_2O_6$
Ortho-phosphoric acid, H_3PO_4
Pyro-phosphoric acid, $H_4P_2O_7$
Meta-phosphoric acid, HPO_3.

Phosphorus pentoxide, P_2O_5, is prepared by igniting phosphorus in excess of dry air or oxygen.

A chunk of white phosphorus is placed in a crucible standing on a tile under a bell-jar and ignited by touching with a hot iron wire—the bell-jar is lifted from time to time to admit fresh air to the burning phosphorus. The white clouds of phosphorus pentoxide settles down to a soft white powder which contains some trioxide. It is purified by heating in a current of dry ozonised air or oxygen when the trioxide is oxidised to P_2O_5—the phosphorus pentoxide sublimes and collects in a well-cooled receiver. $P_4 + 5O_2 = 2P_2O_5$.

It is a white deliquescent powder which sublimes at 250° ; its vapour density corresponds to the formula P_4O_{10}. *An acidic oxide,* it dissolves in *cold* water, giving metaphosphoric acid ; with *boiling* water orthophosphoric acid is produced :

$$P_2O_5+H_2O = 2HPO_3 \;;\quad P_2O_5+3H_2O = 2H_3PO_4.$$

It has great affinity for water, and is the *most effective drying agent ;* thus it dehydrates sulphuric and nitric acids, yielding their anhydrides :

$$H_2SO_4+P_2O_5 = 2HPO_3+SO_3 \;;\; 2HNO_3+P_2O_5 = 2HPO_3+N_2O_5.$$

The phosphoric acids.—Three phosphoric acids are formed by the addition of water to phosphorus pentoxide, which, therefore, is the anhydride of the three acids :

$$P_2O_5 + H_2O = 2HPO_3 \text{ (meta-phosphoric acid) ;}$$
$$P_2O_5 + 2H_2O = H_4P_2O_7 \text{ (pyro-phosphoric acid) ;}$$
$$P_2O_5 + 3H_2O = 2H_3PO_4 \text{ (ortho-phosphoric acid).}$$

When heated to 213°, the ortho-phosphoric acid is slowly transformed into pyro-phosphoric acid, which in its turn is converted into a glassy mass of meta-phosphoric acid, when heated to 316°. Heated still further the meta-phosphoric acid also dehydrates on prolonged heating, yielding some phosphorus pentoxide. The changes are reversible :

$$2H_3PO_4 \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} H_4P_2O_7 \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} 2HPO_3 \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} P_2O_5.$$

Ortho-phosphoric acids, H_3PO_4.—Common phosphoric acid is orthophosphoric acid. It is made : (a) by digesting bone ash with dilute (60%) sulphuric acid in a lead-lined tank for several hours—the mixture is heated by open steam. The bone ash is decomposed by the sulphuric acid, yielding phosphoric acid and calcium sulphate. The insoluble calcium sulphate is fitered off on a bed of coke, and the phosphoric acid solution is evaporated to a thick syrupy liquid of sp. gr. 1.7 containing 85% phosphoric acid.

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

(b) by heating a phosphate mineral with coke and silica in an electric furnace, the resulting phosphorus vapour and CO (*vide* preparation of phosphorus) are burnt to P_2O_5 and CO_2 by admitting air. Water is sprayed in the cooled gases when 85 per cent phosphoric acid is obtained—any mist of phosphoric acid formed is separated by electrostatic precipitation. $P_2O_5+3H_2O = 2H_3PO_4$.

Pure phosphoric acid is obtained by boiling red phosphorus with concentrated nitric acid in a flask fitted with a reflux condenser on a waterbath. A crystal of iodine catalyses the reaction. The resulting solution is concentrated till the temperature rises just to 180°, and then cooled in a vacuum desiccator over concentrated sulphuric acid—the desiccator being placed in a freezing mixture—when colourless crystals of phosphoric acid, m. pt. 42°, deposit.

$$P_4 + 10HNO_3 + H_2O = 4\overset{H_3PO_4}{\cancel{H_3PO_4}} + 5NO + 5NO_2.$$

The phosphates.—Phosphoric acid is *tribasic* and forms three series of salts such as *primary phosphate*, NaH_2PO_4 (monosodium dihydrogen phosphate), *secondary phosphate*, Na_2HPO_4 (disodium monohydrogen phosphate), and tertiary phosphate, Na_3PO_4 (trisodium phosphate).

The three hydrogen ions dissociate in stages from phosphoric acid, the first one readily, the second with difficulty and third in presence of excess alkali only.

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4' \rightleftharpoons 2H^+ + HPO_4'' \rightleftharpoons 3H^+ + PO_4'''.$$

The primary phosphate is *acid* to litmus :

$$NaH_2PO_4 \rightleftharpoons Na^+ + H_2PO_4' \; ; \; H_2PO_4' \rightleftharpoons H^+ + HPO_4''.$$

The secondary phosphate is *faintly alkaline* (practically neutral), the tertiary phosphate *strongly alkaline*, since they are hydrolysed by water : $Na_2HPO_4 + H_2O \rightleftharpoons NaH_2PO_4 + NaOH$;

$$Na_3PO_4 + H_2O \rightleftharpoons Na_2HPO_4 + NaOH.$$

The primary and secondary phosphates decompose on heating with elimination of water :

(i) a primary phosphate yields a metaphosphate :
$NaH_2PO_4 = H_2O + NaPO_3$ (sodium metaphosphate)

(ii) a secondary phosphate yields a pyrophosphate :
$2Na_2HPO_4 = H_2O + Na_4P_2O_7$ (sodium pyrophosphate)

(iii) a tertiary phosphate remains unchanged by heat.

Phosphates containing ammonium radicals, lose both water and ammonia on heating : $(NH_4)_2HPO_4 = HPO_3 + H_2O + 2NH_3$;

$$2MgNH_4PO_4 = Mg_2P_2O_7 + H_2O + 2NH_3$$

$$Na(NH_4)HPO_4 \text{ (microcosmic salt)} = NaPO_3 + H_2O + NH_3.$$

Phosphate	Effect of heat	Phenolphthalein	Methyl orange
(i) Primary NaH_2PO_4	decomposes ; forms metaphosphate	acid	neutral
(ii) Secondary Na_2HPO_4	decomposes ; forms pyrophosphate	neutral	alkaline
(iii) Tertiary Na_3PO_4	does not decompose	alkaline	alkaline

On titration with caustic soda solution phosphoric acid behaves as monobasic with methyl orange which changes colour from orange to just pale yellow at the stage NaH_2PO_4 ; it is however, dibasic with phenolphthalein which turns pink at the stage Na_2HPO_4.

The sodium phosphates are prepared as follows : The secondary phosphate Na_2HPO_4, $12H_2O$, is first made by neutralising phosphoric acid (to which few drops of phenolphthalein are added) with caustic soda till the solution turns pink, and crystallising. The primary phosphate NaH_2PO_4, H_2O, is made by adding correct amount of phosphoric acid to a solution of the secondary phosphate, and evaporating. The tertiary phosphate, Na_3PO_4, $12H_2O$, is made by dissolving the secondary phosphate and excess caustic soda in water and crystallising. On mixing hot strong solutions of sodium phosphate and ammonium chloride, crystals of microcosmic salt, $NaNH_4HPO_4, 4H_2O$, deposit on cooling, $Na_2HPO_4, 12H_2O$ is the *ordinary laboratory sodium phosphate.*

$$\begin{array}{lcccc} & 2NaOH & & NaOH & \\ H_3PO_4 & \longrightarrow & Na_2HPO_4 & & Na_3PO_4 \\ & H_3PO_4 & & NH_4Cl & \\ NaH_2PO_4 \leftarrow & & Na_2HPO_4 & & NaNH_4HPO_4 \end{array}$$

Pyrophosphoric acid crystals, m. p. 61°, are best made by heating H_3PO_4 with phosphorus oxychloride : $5H_3PO_4 + POCl_3 = 3H_4P_2O_7 + 3HCl$, evaporating in a vacuum desiccator and cooling at −10°. It is also formed by heating H_3PO_4 at 213°. Na_2HPO_4 on heating yields $Na_4P_2O_7$ which gives a white precipitate of lead pyrophosphate with lead nitrate solution—this is decomposed by H_2S water, giving pyrophosphoric acid solution :

$$Pb_2P_2O_7 + H_2S = H_4P_2O_7 + 2PbS \text{ (black precipitate)}.$$

Magnesia mixture (a solution of magnesium chloride containing ammonia and ammonium chloride) yields with a solution of a orthophosphate a white crystalline precipitate of magnesium ammonium phosphate $MgNH_4PO_4,6H_2O$, which on heating gives magnesium pyrophosphate. This reaction is used in the estimation of phosphate and magnesium : $2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O$.

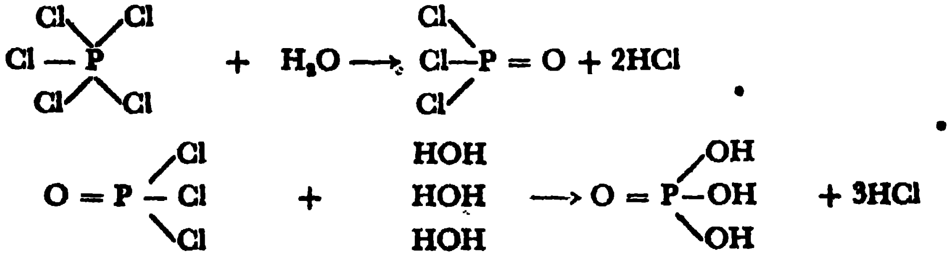
Metaphosporic acid, HPO_3, is obtained as a glassy mass by heating H_3PO_4 or $H_4P_2O_7$ at 316° : $H_3PO_4 = HPO_3 + H_2O$. The acid thus formed, is polymerised $(HPO_3)n$.

NaH_2PO_4 in heating yields $NaPO_3$ which gives a white precipitate of lead metaphosphate with lead nitrate solution—this with H_2S water gives metaphosphoric acid which has the simple formula HPO_3 : $Pb(PO_3)_2 + H_2S = 2HPO_3 + PbS$. HPO_3 is best made by the action of $POCl_3$ on H_3PO_4.

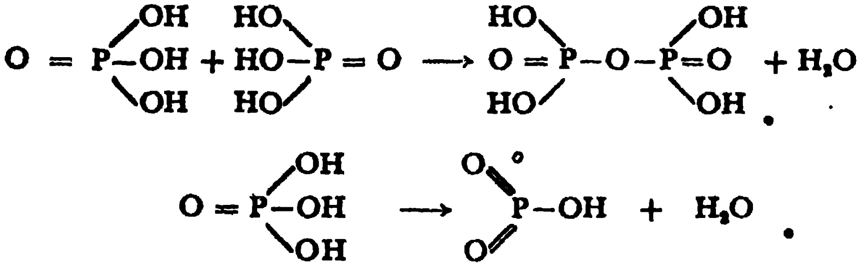
$$2H_3PO_4 + POCl_3 = 3HPO_3 + 3HCl.$$

Calgon.—Sodium hexa-metaphosphate $(NaPO_3)_6$, is made as a clear glass, soluble in water by fusing and rapidly cooling either NaH_2PO_4 or the microcosmic salt. It is used for softening water (page 192).

Structure of phosphoric acids.—The hydrolysis of PCl_5 shows the structure of ortho-phosphoric acid. PCl_5 on partial hydrolysis yields phosphorus oxychloride, $POCl_3$, which is then further hydrolysed to H_3PO_4.



The pyro- and meta-phosphoric acids are derived from the ortho-acid by elemination of water :



Tests for phosphate.—(i) *Cobalt nitrate test.*—Heated on charcoal with a drop or two of cobalt nitrate solution in the oxidising flame a phosphate yields a *blue mass.*

(ii) *Ammonium molybdate test.*—On adding few drops of a orthophosphate solution to an excess of ammonium molybdate solution acidified with concentrated nitric acid a *canary-yellow* precipitate of ammonium phosphomolybdate slowly deposits in the cold and rapidly at 60°—65°. Pyro- and meta-phosphates also give this test on heating for some time. Arsenates also respond to this test but *only on boiling.*

$$Na_2HPO_4 + 12(NH_4)_2MoO_4 \text{ (ammonium molybdate)} + 23HNO_3$$
$$= (NH_4)_3[PMo_{12}O_{40}] \text{ (ammonium phosphomolybdate)} + 2NaNO_3 + 21NH_4NO_3 + 12H_2O.$$

Reagent	Orthophosphate	Pyrophosphate	Metaphosphate
(i) $AgNO_3$ soln.	Yellow ppt.	White ppt.	White ppt.
(ii) Albumin + dil. acetic acid	No coagulation	No coagulation	Coagulation
(iii) Magnesia mixture	White ppt. insoluble in excess of the reagent.	White ppt., soluble in excess, but reappears on boiling	No ppt., even on boiling.
(iv) $BaCl_2$ solution	No ppt. ; white ppt. if alkaline.	No. ppt.; white ppt. if alkaline.	White ppt., in acid solution.

Phosphorus trioxide, P_2O_3, is formed by burning phosphorus in a limited supply of air : $P_4 + 3O_2 = 2P_2O_3$.

A slow stream of air is drawn over sticks of white phosphorus gently burnt in a tube (fig. 152)—the vapour of the oxides formed passes through a metal condenser, surrounded by hot water at 60°, and also containing a plug of glass wool which arrests the less volatile P_2O_5 which is also formed, and allows the more volatile P_2O_3 to pass through, which is condensed in a receiver cooled in ice. The air is aspirated through the apparatus by a water-pump.

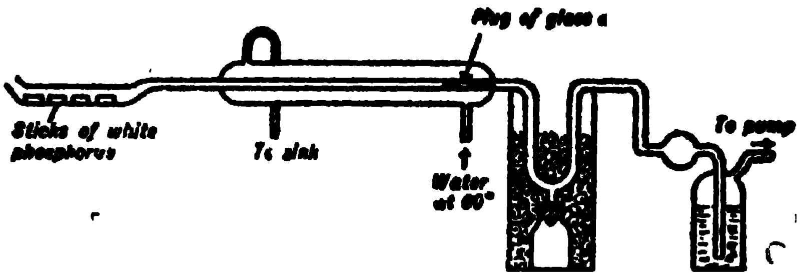


Fig. 152

Phosphorus trioxide, is a white crystalline solid, m.p. 23.8°, and b. p. 175°. Its vapour density shows the formula to be P_4O_6. It dissolves in cold water, forming phosphorous acid of which it is the anhydride ; with hot water it gives phosphine and phosphoric acid :

$$P_2O_3 + 3H_2O = 2H_3PO_3 \ ; \ 2P_2O_3 + 6H_2O = PH_3 + 3H_3PO_4.$$

Phosphorous acid, a white solid, m. p. 73.6°, may also be obtained by the hydrolysis of phosphorus trichloride.

$$PCl_3 + 3HOH = 3HCl + H_3PO_3.$$

It has strong *reducing properties*. It gives a black precipitate of metallic silver with silver nitrate solution :

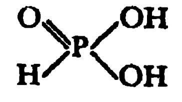
$$H_3PO_3 + 2AgNO_3 + H_2O = H_3PO_4 + 2HNO_3 + 2Ag.$$

It also precipitates gold and copper from solutions of their salts, and reduces mercuric chloride to mercurous chloride.

$$H_3PO_3 + 2HgCl_2 + H_2O = H_3PO_4 + Hg_2Cl_2 + 2HCl.$$

It is a *dibasic acid ;* it decomposes on heating into PH_3 and H_3PO_4 :

$$4H_3PO_3 = PH_3 + 3H_3PO_4.$$

Its structure is  the reducing property being due to the hydrogen atom directly linked to phosphorus.

Hypophosphorous acid H_3PO_2, colourless crystals, m. p. 26.5°. A solution of barium hypophosphite is prepared by heating white phosphorus with baryta water in a flask from which the air is displaced by carbon dioxide (*cf.* preparation of PH_3).

$$2P_4 + 3Ba(OH)_2 + 6H_2O = 2PH_3 + 3Ba(H_2PO_2)_2.$$

The excess of baryta is precipitated as barium carbonate by passing CO_2, and filtered. The filtrate is decomposed by calculated amount of dilute H_2SO_4.

$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 + 2H_3PO_2.$$

The insoluble $BaSO_4$ is filtered off, and the filtrate containing hypophosphorous acid, is carefully evaporated below 130° to a syrup, and cooled in freezing mixture, when it crystallises.

The acid or its salts decompose on heating, evolving phosphine :

$$2H_3PO_2 = H_3PO_4 + PH_3\ ;\quad 2NaH_2PO_2 = Na_2HPO_4 + PH_3.$$

It is a *powerful reducing agent.* Silver nitrate gives a black precipitate of silver :

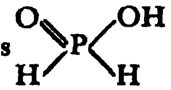
$$H_3PO_2 + 2H_2O + 4AgNO_3 = 4Ag + H_3PO_4 + 4HNO_3.$$

Copper salts give on warming a red precipitate of cuprous hydride which evolves hydrogen with strong HCl (a distinction from phosphorous acid).

$$3H_3PO_2 + 3H_2O + 2CuSO_4 = 2CuH + 3H_3PO_3 + 2H_2SO_4$$

It reduces mercuric chloride to a black mass of metallic mercurry.

$$H_3PO_2 + 2H_2O + 2HgCl_2 = H_3PO_4 + 2Hg + 4HCl.$$

It is a *monobasic* acid and its structure is , the reducing property is due the hydrogen atoms directly linked to phosphorus. Calcium hypophosphite is used medicinally as nerve tonics.

Phosphorus tetroxide.—P_2O_4, a colourless solid, is formed by heating P_2O_3 in a sealed tube at 440° : $4P_2O_3 = 3P_2O_4 + 2P$ (red P). It is also made by heating a mixture of trioxide and pentoxide in a sealed tube to 290° : $P_2O_3 + P_2O_5 = 2P_2O_4$. It dissolves in water, forming phosphorus and phosphoric acids :

$$P_2O_4 + 3H_2O = H_3PO_3 + H_3PO_4.$$

Superphosphate of lime.—An important phosphatic fertiliser, it is made by the action of chamber acid (65 to 70 p.c. H_2SO_4) on mineral tricalcium phosphate such as *apatite* or *phosphorite rock,* when soluble monocalcium phosphate is formed :

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O = Ca(H_2PO_4)_2 + 2(CaSO_4, 2H_2O).$$

The mixture of the monocalcium phosphate and calcium sulphate constitutes the superphosphate.

The finely ground rock is macerated with two-thirds of its weight of the chamber acid in a cast-iron mixer fitted with revolving blades for 2 minutes and then quickly dumped for 24 hours in a closed den or pit below, where reaction occurs with a rise in temperature to 100°, and evolution of such gases as CO_2, HCl and SiF_4, which escape through a vent. The mass is then removed to the storage piles, where it is allowed to *cure* for 8 to 10 weeks before use.

Other important phosphatic fertilisers are bone meal and basic slag.

Manufacture of matches.—The chief use of phosphorus is in match industry. Red phosphorus and phosphorus sulphide are used for the purpose—the use of yellow phosphorus being prohibited by law, due to its poisonous nature. Workmen exposed to its vapour are liable to the decay of bones, particularly of the jaw, and develop the disease of jaw bones (phossy-jaw).

'Strike anywhere' matches.—They are prepared by dipping thin strips of wood into a paste containing phosphorus sulphide, lead oxide and potassium chlorate plus some powdered glass and glue. The strips are ignited by friction against a rough surface—this is a *disadvantage.*

Safety matches.—In preparing safety matches strips of wood are tipped with a paste containing potassium chlorate, potassium dichromate, MnO_2, sulphur, oxide of iron, powdered glass, *gum* and *glue,* but no phosphorus. The sticks are ignited by rubbing against a strip of paper (attached to the match box) coated with a paste of red phosphorus, antimony sulphide, powdered glass and glue.

The heat of friction brings about the oxidation of phosphorus by potassium chlorate—the spark being communicated to the sticks which ignite. The sticks are previously soaked in borax solution to prevent glowing aeftr the flame is extinguished.

Exercises

1. Describe the preparation of white phosphorus. How is it converted to red phosphorus ? Compare the porperties of these two varieties of phosphorus. What happens when (a) each form of phosphorus is boiled with caustic soda solution, (b) red phosphorus is heated with concentrated nitric acid, and (c) slow stream of chlorine is passed through white phosphorus melted under water ? Describe what happens when red phosphorus is allowed to act on iodine suspended in water.

2. How is phosphine prepared ? State the percautions usually taken and give the equation for the reaction. State the chief properties of this gas and compare them with those of ammonia. *Bombay '53*

3. Describe in outline the preparation of phosphorus trioxide and pentoxide. Give a short account of the various acids which may be derived from them. How would you distinguish between them ? How many potassium salts of phosphoric acid are there, and what is the reaction of their aqueous solution ? Describe the action of heat on them.

4. How are the chlorides of phosphorus obtained ? What is the action of water on these compounds ? What happens when phosphorus pentachloride is heated ? What is the action of heat on monosodium hydrogen phosphate ?

5. Starting from bone ash, how will you prepare (a) phosphorus, (b) phosphorus trioxide, (c) phosphorus pentoxide, (d) phosphine ? Give equations. *Ajmer Inter.*

Arsenic

Occurrence.—Arsenic is widely distributed in nature in the combined state. Its chief minerals are : *arsenical pyrites* or *mispickel*, FeAsS, *realgar*, As_2S_2, and *orpiment*, As_2S_3. Iron pyrites and other sulphide ores often contain arsenic. The arsenical minerals on roasting yield white fumes of arsenous oxide, As_2O_3, which may be condensed in flues as a powder, known in commerce as *white arsenic.*

Preparation.—Arsenic is prepared by heating arsenious oxide with charcoal in clay crucible covered with an iron cone into which the arsenic sublimes : $As_2O_3 + 3C = 3CO + 2As$. It may also be obtained by distilling arsenical pyrites : $FeAsS = FeS + As$.

Arsenic exists in three allotropic forms : (i) *yellow arsenic* corresponding with white phosphorus, soluble in carbon disulphide, an unstable form produced by rapidly chilling the arsenic vapour ; (ii) *black arsenic*, less stable than grey arsenic, and insoluble in carbon disulphide, it deposits as a black mirror on the cooler part of a tube when the grey arsenic is heated in a current of hydrogen and (iii) *grey arsenic*, the stable and common form, insoluble in carbon disulphide.

Properties.—(i) Grey arsenic forms steel-grey, brittle crystals with a *metallic lustre* and *marked conductivity*. It sublimes on heating to give a yellow vapour with a *garlic smell.* Like phosphorus, it is tetratomic (As_4) in the vapour state.

(ii) It burns in air with a blue, livid flame, giving arsenious oxide : $4As + 3O_2 = 2As_2O_3$. It ignities spontaneously in chlorine, forming the trichloride : $2As+3Cl_2 = 2AsCl_3$.

(iii) It is only attacked by oxidising acids, and therein it resembles a non-metal. Hot dilute HNO_3 slowly oxidises arsenic to arsenious acid H_3AsO_3, while the hot conc. HNO_3 converts it to arsenic acid H_3AsO_4. Hot concentrated H_2SO_4 oxidises it to arsenious oxide.

(iv) It is attacked by fused alkalis, forming arsenites, but not by aqueous alkalis : $2As + 6NaOH = 2Na_3AsO_3 + 3H_2$.

Arsine, AsH_3 is conveniently prepared by the action of warm water upon aluminium arsenide : $AlAs+3H_2O = Al(OH)_3+AsH_3$. *Pure arsine* is produced by the action of dilute HCl upon zinc arsenide. Arsine is also produced by the action of *nascent* hydrogen on a soluble arsenic compound.

$$Zn_3As_2+6HCl = 3ZnCl_2+2AsH_3 ; \quad As_2O_3+12H = 2AsH_3+3H_2O.$$

A *highly poisonous* colourless gas with a garlic smell, it is insoluble in water and has no *basic properties.* It forms no compound similar to phosphonium compounds. It decomposes into its elements on gentle heating. *It is a reducing agent.* It gives a black precipitate of silver with *dilute* silver nitrate solution.

$$AsH_3 + 6AgNO_3 + 3H_2O = H_3AsO_3 + 6HNO_3 + 6Ag.$$

Arsenious oxide, white arsenic, As_2O_3, is produced commercially by roasting arsenical ores, such as pyrites, and condensing the volatile arsenious oxide in flues as a white powder.

This oxide is slightly soluble in water—the solution is feebly acid to litmus due to the formation of arsenious acid.

$$As_2O_3 + 3H_2O \rightleftharpoons 2H_3AsO_3$$

But it readily dissolves in solutions of alkalis or carbonates to yield arsenites, and in concentrated HCl to yield arsenious chloride, and hence the oxide is amphoteric in character ;

$$As_2O_3+6NaOH = 2Na_3AsO_3 + 3H_2O ;$$
$$As_2O_3+6HCl = 2AsCl_3+3H_2O.$$

It is a reducing agent. It reduces iodine to HI.

$$As_2O_3 + 2I_2 + 2H_2O \rightleftharpoons As_2O_5 + 4HI.$$

The reaction goes to completion *in presence of sodium bicarbonate* which removes HI, since unlike NaOH or Na_2CO_3 sodium bicarbonate is without action upon iodine.

It also acts as an oxidising agent. It is reduced to arsenic when heated with charcoal, and in solution by stannous chloride,

$$As_2O_3 + 3SnCl_2 + 6HCl = 2As + 3SnCl_4 + 3H_2O,$$

and also when boiled with hydrochloric acid and copper foil :

$$As_2O_3 + 6HCl + 6Cu = 2As + 6CuCl + 3H_2O.$$

If the copper foil is washed, dried and heated, white sublimate of As_2O_3 is formed (*Reinsch's test*).

Arsenious oxide is used in the preparation of pigments and enamels ; in glass making ; in taxidermy for preserving skins ; as a poison for vermin ; as a weedkiller ; in small doses in medicine as a tonic and in skin diseases.

Arsenic oxide, As_2O_5, is obtained as a white deliquescent solid by oxidising arsenious oxide with concentrated HNO_3 or chlorine :

$$As_2O_3+2HNO_3 = As_2O_5+N_2O_3+H_2O.$$

It dissolves in water, giving arsenic acid ; $As_2O_5 + 3H_2O = 2H_3AsO_4$, and in alkalis to give arsenates—arsenates are analogous to and isomorphous with phosphates. It is an oxidising agent, and is reduced to arsenious acid by hydriodic acid : $H_3AsO_4 + 2HI \rightleftharpoons H_3AsO_3 + I_2 + H_2O$.

Arsenites and arsenates.—Sodium arsenite is obtained by dissolving As_2O_3 in caustic soda solution. With silver nitrate solution it gives a *yellow* precipitate of silver arsenite, soluble in acetic acid (cf. Ag_3PO_4 which is insoluble.)

$$Na_3AsO_3+3AgNO_3 = Ag_3AsO_3+3NaNO_3.$$

With copper sulphate solution it gives a green precipitate of cupric arsenite (*Scheele's green*), $Cu_3(AsO_3)_2,2H_2O$.

Sodium arsenate is made by fusing sodium arsenite with sodium nitrate. It is used in calico-printing. It gives a light *chocolate* precipitate of silver arsenate with silver nitrate solution, insoluble in acetic acid : $Na_3AsO_4 + 3AgNO_3 = Ag_3AsO_4 + 3NaNO_3$. It liberates iodine from an acidified solution of potassium iodide.

$$H_3AsO_4 + 2HI \rightleftharpoons H_3AsO_3 + I_2 + H_2O.$$

Arsenious chloride, $AsCl_3$, is prepared by dissolving As_2O_3 in hot and strong HCl or by distilling a mixture of As_2O_3 with common salt and strong H_2SO_4. $As_2O_3+6HCl \rightleftharpoons 2AsCl_3+3H_2O$. A poisonous, oily liquid, b.p. 130°, it is *hydrolysed* by water to arsenious oxide—the reaction is *reversible.*

Sulphides of arsenic occur native as the yellow and red mineral *orpiment,* As_2S_3, and *realgar,* As_2S_2, respectively. Realgar is used as a pigment and in pyrotechny.

Arsenic trisulphide is precipitated as a yellow powder by passing H_2S through an acid solution of arsenious oxide : $As_2O_3 + 3H_2S = As_2S_3 + 6HCl$. Insoluble in strong HCl, it dissolves in alkalis, giving arsenite and thioarsenite, from which it is precipitated by the addition of acids.

$$As_2S_3 + 6KOH = K_3AsO_3 + K_3AsS_3 + 3H_2O\ ;$$
$$K_3AsO_3 + K_3AsS_3 + 6HCl = 6KCl + 3H_2O + As_2S_3$$

It also dissolves in yellow ammonium sulphide, giving thioarsenate which precipitates the pentasulphide on acidification :

$$As_2S_3 + 3(NH_4)_2S + 2S = 2(NH_4)_3AsS_4\ ;$$
$$2(NH_4)_3AsS_4 + 6HCl = 6NH_4Cl + 3H_2S + As_2S_5$$

On passing H_2S through a solution of arsenic acid the latter is reduced to arsenious acid, and a white precipitate of sulphur is formed—on further passing the gas, arsenious sulphide is deposited.

$$H_3AsO_4 + H_2S = H_3AsO_3 + H_2O + S\ ;\ 2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O.$$

Tests.—(i) **Mirror test.**—On heating an arsenic compound with soda-lime and potassium cyanide in a bulb-tube a black mirror of arsenic with a garlic smell is deposited on the cold tube further on.

(ii) **Marsh's test.**—In this test the arsenic compound is reduced to arsine by nascent hydrogen. Some granules of zinc (arsenic free) and the arsenic compound are taken in a flask (fig. 153) fitted with a thistle funnel and a delivery tube—on the addition of pure dilute H_2SO_4, arsine is produced, which passes out of the delivery tube. Arsine is decomposed on heating the tube and a black mirror of arsenic is deposited beyond the heated portion. This is a very delicate test and is used to detect arsenic in trace.

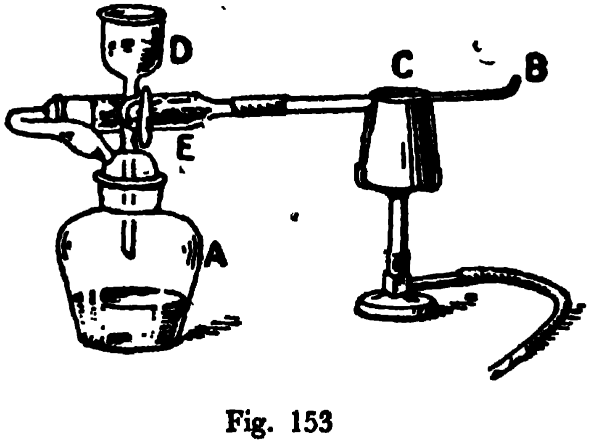


Fig. 153

(iii) **Fleitmann's test.**—When an arsenious compound is heated with zinc dust and caustic soda, arsine is evolved which stains black a paper soaked in silver nitrate solution.

(iv) **Wet tests.**—(a) Silver nitrate solution gives a *yellow* and a *chocolate* precipitate with neutral solution of arsenite and arsenate respectively—the precipitates are soluble in nitric acid solution. (b) Magnesia mixture gives a white precipitate of magnesium ammonium arsenate, $MgNH_4AsO_4$, with an arsenate solution only. (c) Ammonium molybdate in presence of conc. HNO_3 gives a yellow ppt. with a boiling solution of an arsenate (*cf. phosphate*).

Antimony

Preparation.—The principal ore of antimony is *stibnite* Sb_2S_3. The metal is prepared by reducing the ore with iron at a red heat : $Sb_2S_3 + 3Fe = 2Sb + 3FeS$, or by roasting stibnite to the oxide and then reducing with coke :

$$2Sb_2S_3+9O_2 = 2Sb_2O_3+6SO_2 \ ; \quad Sb_2O_3+3C = 2Sb+3CO.$$

Properties.—(i) A brittle, silver-white, lustrous metal, antimony *expands on solidification,* and hence useful in casting. It exists in three allotropic forms : *metallic antimony,* the common form, *yellow antimony* (soluble in carbon disulphide), and *black antimony* (inflammable in air).

(ii) Stable in air, it burns when heated, forming a mixture of Sb_2O_3 and Sb_2O_4. It also burns spontaneously in chlorine, forming the penta-chloride, $SbCl_5$. $2Sb + 5Cl_2 = 2SbCl_5$.

(iii) It is not acted upon by water or dilute acids. It decomposes steam at a red heat, and *is oxidised to Sb_2O_5 by concentrated HNO_3*, showing its non-metallic character. It dissolves in hot concentrated HCl in presence of air, forming the chloride, and also in hot concentrated H_2SO_4, forming the sulphate.

$$2Sb + 6H_2SO_4 = Sb_2(SO_4)_3 + 3SO_2 + 6H_2O.$$

It dissolves readily in aqua regia, forming the pentachloride, $SbCl_5$.

Uses.—The chief use of antimony is in making alloys : *type metal* (Pb 55 : Sb 30 : Sn 15) ; *antifriction metal* (Pb 75 : Sb 15 : Sn 8 : Cu 2) used for bearing of machinery ; *Britannia metal* (Sb 5 : Sn 94 : Cu 1).

Stibine.—SbH_3 is prepared by the action of dilute HCl upon an alloy of magnesium and antimony : $Mg_3Sb_2 + 6HCl = 3MgCl_2 + 2SbH_3$, and by the action of nascent hydrogen on an antimony compound in acid solution.

A neutral, colourless, poisonous gas with an unpleasant smell, fairly soluble in water, it is readily decomposed into its elements by heat. It is a reducing agent. It gives a black precipitate of silver antimonide with silver nitrate solution. (e.g. arsine) : $SbH_3 + 3AgNO_3 = Ag_3Sb + 3HNO_3$.

The precipitate is rapidly decomposed by excess of silver nitrate into a black mass of silver and antimony trioxide.

$$2Ag_3Sb + 6AgNO_3 + 3H_2O = 12Ag + Sb_2O_3 + 6HNO_3$$

Antimony oxides.—Antimony forms the oxides Sb_2O_3, Sb_2O_4 and Sb_2O_5.

Antimony trioxide, Sb_2O_3, is made by burning the metal in air and by the hydrolysis of antimony trichloride : $2SbCl_3 + 3H_2O \rightleftharpoons Sb_2O_3 + 6HCl$.

A white powder, it becomes yellow on heating. An amphoteric oxide insoluble in water, it dissolves in alkalis giving antimonites, and in acids, producing salts.

Antimony tetroxide, Sb_2O_4, is produced by heating Sb_2O_3 above 400° in air. It imparts an acid reaction to water.

Antimony pentoxide, Sb_2O_5, is obtained by the hydrolysis of penta chloride or by the action of conc. HNO_3 upon antimony or its lower oxide. An insoluble yellow powder and acidic oxide, it gives rise to antimonic acid and antimoniates.

Antimony chlorides.—Antimony trichloride, $SbCl_3$, a deliquescent, white solid, is prepared by dissolving antimony trisulphide in concentrated HCl and evaporating. It is *reversibly* hydrolysed by water, precipitating the white oxychloride :

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl.$$

Antimony pentachloride, $SbCl_5$, a heavy fuming liquid, is prepared by passing chlorine into molten trichloride. It liberates iodine from potassium iodide. $SbCl_5 + 2KI = SbCl_3 + 2KCl + I_2$.

Antimony sulphides.—Antimony form two sulphides Sb_2S_3 and Sb_2S_5. Antimony trisulphide is obtained as an orange yellow powder by passing H_2S through an acid solution of antimony trichloride.

Just like As_2S_3, it dissolves on caustic alkalis, in alkali sulphide and in yellow ammonium sulphide. But unlike As_2S_3, *it is insoluble in ammonium carbonate.* It dissolves in strong HCl, whereas arsenic sulphide is insoluble.

It burns when heated in air, and hence its use in fire works, percussion caps and match heads. It also finds use as a pigment and in the vulcanisation of rubber.

Tartar emetic, potassium antimonyl tartrate $K(SbO)\ C_4H_4O_6$, is made by boiling antimony oxide and cream of tartar and is used in medicine and as a mordant.

Tests.—(i) An antimony compound, mixed with fusion mixture and heated on charcoal in the reducing flame, gives a white, lustrous, brittle bead with a white incrustation.

(ii) H_2S gives an orange yellow precipitate of antimony trisulphide with an acid solution of an antimony salt.

Bismuth

Preparation.—Bismuth is often found native. It also occurs as *bismuth ochre*, Bi_2O_3, *bismuthite* or *bismuth spar* $(BiO)_2CO_3$, and *bismuthinite* or *bismuth glance*, Bi_2S_3.

The metal is obtained from native bismuth by liquation—the ore is heated in a sloping iron tube, when bismuth melts (m. p. 271°) and flows away. The metal is refined by dissolving in dilute HNO_3, pouring the solution into much water, calcining the precipitated basic nitrate, and reducing the oxide with charcoal and a flux.

Properties.—(i) An easily fusible, brittle, silver-white metal bismuth burns to the trioxide, Bi_2O_3, when heated in air.

(ii) It catches fire in chlorine forming the trichloride, $BiCl_3$, and decomposes steam slowly at a red heat.

(iii) It is not attacked by dilute acids, except HNO_3, which converts it into nitrate. Boiling concentrated H_2SO_4 converts in into the sulphate, $Bi_2(SO_4)_3$, sulphur dioxide being evolved.

Bismuth is used in making fusible alloys : *Rose's metal* (m. p. 93.75°) contains Bi (2 parts), Pb (1 part), and Sn (1 part) and *Wood's fusible metal* (m.p. 71°) contains Bi (4 parts), Pb (2 parts), Sn (1 part) and Cd (1 part).

Bismuthine, BiH_3, an unstable gas is obtained by the action of HCl upon an alloy of magnesium and bismuth. It is slightly acidic and is soluble in alkali.

Bismuth oxides.—Bismuth forms the oxides BiO, Bi_2O_3, Bi_2O_4 and Bi_2O_5.

Bismuth monoxide, BiO, a black powder, is obtained by reducing Bi_2O_3 with carbon monoxide : $Bi_2O_3 + CO = 2BiO + CO_2$. A basic oxide, it reacts with acids, giving metallic bismuth and a tervalent salt.

Bismuth trioxide, Bi_2O_3, a yellow powder, is obtained by burning the metal or by igniting bismuth subnitrate. It is readily reduced to the metal by heating with carbon or hydrogen. It is predominently basic in properties—its slight solubility in strong alkali shows that it is also feebly acidic.

Bismuth tetroxide, Bi_2O_4, a brown powder, is produced by the action of chlorine on an alkaline suspension of bismuth trioxide. It loses oxygen on heating and is reduced when warmed with strong HCl or H_2SO_4, giving chlorine or oxygen respectively : $Bi_2O_4 + 8HCl = 2BiCl_3 + 4H_2O + Cl_2$.

Bismuth pentoxide, Bi_2O_5, a brown powder, is obtained by drying meta bismuthic acid, $HBiO_3$, produced by acidifying (with dilute nitric acid) potassium bismuthate, $KBiO_3$, which is precipitated by the prolonged action of chlorine on an alkaline solution of bismuth trioxide. When heated and when treated with acids, it behaves like the tetroxide : $Bi_2O_5 + 3H_2SO_4 = Bi_2(SO_4)_3 + 3H_2O + O_2$.

Bi_2O_5 is also precipitated by the hydrolysis of potassium bismuthate, $KBiO_3$, formed by the fusion of Bi_2O_3 with caustic potash in air. The higher oxides of bismuth, therefore, show *acidic* properties. The bismuthates are used as oxidising agents.

Bismuth chloride.—$BiCl_3$, a white crystalline solid, is prepared by burning bismuth in chlorine. It is reversibly hydrolysed by much water, precipitating white bismuth oxychloride : $BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$.

Bismuth sulphide, Bi_2S_3, is obtained as a black precipitate passing H_2S through an acid solution of the chloride. It readily dissolves in nitric acid, but unlike the sulphides of As, Sb and Sn, it is insoluble in alkalis and yellow ammonium sulphide.

Bismuth nitrate, $Bi(NO_3)_3, 5H_2O$, a white crystalline deliquescent solid, is obtained by dissolving bismuth, its oxide or carbonate in nitric acid and crystallising. It dissolves in water in presence of nitric acid. On the addition of much water, an insoluble basic nitrate, known as *bismuth subnitrate*, $BiONO_3$, precipitates.

$Bi(NO_3)_3 + H_2O \rightleftharpoons BiONO_3 + 2HNO_3$. The sub-nitrate is used as a medicine in diarrhoea and in gilding *porcelain.*

Bismuthyl carbonate, $(BiO)_2CO_3$, is precipitated by the addition of sodium carbonate to a solution of bismuth nitrate. It is the only carbonate formed by the elements of this family and serves to show the superior metallic character of bismuth. The readiness with which bismuth forms basic salts shows that its oxide is not a strong base.

Tests.—(i) A bismuth compound, mixed with fusion mixture and heated on charcoal in the reducing flame, yields a white, lustrous, brittle bead with an orange-yellow incrustation.

(ii) A solution of a bismuth salt gives a white precipitate of a basic salt on dilution with water : $BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$.

Comparison of N, P, As, Sb and Bi—(i) **Elecctrochemical character.**—These elements, belonging to the 5th group in the periodic table, show a regular gradation in properties with a progressive decrease of non-metallic character from the typical non-metals N_2 and P to the typical metal Bi ; As and Sb are *metalloids.*

(ii) **Physical properties.**—These elements have low m. p's. and (except Sb and Bi) low b.p.'s Their molecules contain more than one atom in the vapour state.

	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Atomic weight	14.008	30.98	74.91	121.76	209.0
Density of solid	1.0265	1.83	5.73	6.71	9.80
Melting point	210°	44.1°	814.5°	630.5°	271°
Boiling point	196°	287°	615°	1380°	1480°
Molecule (vapour)	N_2	P_4	As_4	Sb_2	Bi_2

(iii) **Allotropy.**—These elements exist in allotropic forms. Active nitrogen is an allotrope of ordinary nitrogen. Allotropes of phosphorus are yellow P (soluble in CS_2), red P, and black P (feeble conductor of electricity). Allotropes of As are yellow As (soluble in CS_2), black As, and gray As (marked lustre and conductivity). Yellow Sb is soluble in CS_2, other forms black antimony and metallic antimony. Grey As, antimony and bismuth show metallic lustre and conductivity.

(iv) **Valency.**—The valencies are generally 3 and 5—hydrogen valency 3 as in NH_3, and PH_3 and the highest oxygen valency 5 as in N_2O_5 and P_2O_5.

(v) **Chemical properties.**—Nitrogen is inert, while phosphorus is very active and catches fire in air. As, Sb and Bi burn to their oxides when heated in air. Less electropositive than hydrogen, P, As, Sb and Bi are not attacked by non-oxidising acids HCl and dil. H_2SO_4. Hot concentrated HNO_3 oxidises P, As and Sb to P_2O_5, As_2O_5 and Sb_2O_5 (showing non-metallic character of Sb) and Bi to bismuth nitrate, and concentrated $H_2\ SO_4$ converts As to As_2O_3, and Sb and Bi to their sulphates.

(vi) **Hydrides.**—The elements form gaseous hydrides of the type NH_3—their stability, basic character, and solubility in water decrease steadily from NH_3 to bimuthine BiH_3. NH_3 is stable, distinctly basic, and highly soluble in water—solution is alkaline ; PH_3 is less stable, faintly basic and slightly soluble in water—solution is neutral to litmus. AsH_3, SbH_3, BiH_3 are all neutral and insoluble in water. AsH_3 and SbH_3 are readily decomposed by heat, while BiH_3 is very unstable. These hydrides are reducing agents—NH_3 at high temperature only. Besides NH_3, nitrogen froms hydrazine, N_2H_4 ; a basic liquid, and the hydrazoic acid N_3H. Phosphorus also forms P_2H_4, a neutral volatile liquid and an analogue of N_2H_4.

(vii) **Oxides and oxyacids.**—These elements form oxides of the type N_2O_3 whose acidic character decreases from N_2O_3 to Bi_2O_3. N_2O_3 and P_2O_3 are acidic and with water form nitrous and phosphorus acids respectively. As_2O_3 though mainly acidic forming H_3AsO_3 with water shows feeble basic properties. Sb_2O_3 is also amphoteric like As_2O_3. Bi_2O_3 is mainly basic but shows very feeble acid properties. They all form typical acidic pentoxides of the type P_2O_5—acid property diminishes gradually such that Bi_2O_5 is only feebly acidic. Pentoxides are the anhydrides of the corresponding oxyacids HNO_3, H_3PO_4, H_3AsO_4 and H_3SbO_4, only bismuthates (acid not isolated) are known, e.g., $NaBiO_3$. These elements also form oxide of the type N_2O_4 ; N_2O_4, P_2O_4, As_2O_4 and Sb_2O_4 are mixed anhydride, while Bi_2O_4 is a mixed oxide. Nitrogen also forms two neutral oxides N_2O and NO.

N, P, and As resemble non-metals in not forming salts. Sb forms unstable sulphate, while Bi forms salts which are readily hydrolysed.

(viii) **Chlorides.**—The chlorides are NCl_3, PCl_3, PCl_5, $AsCl_3$, $SbCl_3$, $SbCl_5$, and $BiCl_3$. They are decomposed by water—tendency towards hydrolysis decrease with increasing metallic character. NCl_3 (explosive liquid), PCl_3 (liquid) and PCl_5 (solid) are *irreversibly* hydrolysed by water.

$$NCl_3 + 3H_2O = NH_3 + 3HOCl\ ;\quad PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

Chlorides of As, Sb and Bi and but *reversibly* hydrolysed by water.

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl\ ;\quad BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl.$$

(ix) **Metallic compounds.**—All these elements form compounds with metals, e.g., Mg_3N_2, Ca_3P_2, Na_3As, Mg_3Sb_2 and Mg_3Bi_2.

(x) **Sulphides.**—Sulphides of nitrogen and phosphorus, e.g., N_2S_5 (deep red liquid) and P_2S_5 (pale yellow solid), are readily hydrolysed by water :

$$P_2S_5 + 8H_2O = 2H_3PO_4 + 5H_2S.$$

As and Sb form the tri- and pentasulphides, e.g.; As_2S_3, As_2S_5 and Sb_2S_3, Sb_2S_5, but bismuth only the trisulphide, Bi_2S_3. Arsenic and antimony sulphides are soluble in dilute alkali hydroxide, forming thio- and oxysalts, and in alkali sulphide yielding thiosalts. But bismuth sulphide is insoluble in these reagents.

Exercises,

1. Describe the preparation of arsenic. Discuss the family relationship of phosphorus, arsenic, antimony and bismuth. *Bombay '53*

2. What are the chief sources of white arsenic ? How this may be converted into arsenic, arsenic trichloride, arsenic acid, arsenious sulphide ? *Punjab '45*

3. Describe the preparation of arsenic, and compare its properties with those of ammonia and phosphine.

4. Explain with equations what happens when : (a) arsine is passed into silver nitrate solution, (b) bismuth chloride is poured into water, (c) arsenic trisulphide is digested with caustic alkali and then acidified, (d) potassium iodide is added to sodium arsenate solution, (e) arsenious oxide is boiled with hydrochloric acid and copper foil.

XXV

Boron

Symbol B. Atomic weight 10.82. Atomic number 5. Density 2.34. Atomic volume 4.62. M. pt. 2300°C. B. pt. 2550°C. Valency 3.

History and occurrence.—The use of borax as a flux and a glaze was known from early times. But the element boron was isolated by the electrolysis of moist boric acid by Davy in 1807, who also made it in 1808 by heating fused boric acid (i.e., boron trioxide) with potassium.

Boron does not occur in the free state but only as (i) **boric acid** H_3BO_3 in the hot springs of Tuscany, and (ii) **borates**—several mineral borates are : (a) **tincal** or native borax, $Na_2B_4O_7$, $10H_2O$, in India, Tibet, Ceylon and California, (b) **colemanite,** $Ca_2B_6O_{11}$, $5H_2O$ in California and Asia Minor. (c) **ulexite** or **boro-natro calcite** $Na_2B_4O_7$, $Ca_2B_6O_{11}$, $16H_2O$ in Chile, and (d) **boracite** $MgCl_2$, $2Mg_3B_8O_{15}$ in Stassfurt deposits.

Preparation.—Boron may be obtained in two forms, *amorphous* and *crystalline.* Amorphous boron is prepared : (a) by heating boron trioxide with sodium, potassium, magnesium or aluminium, or (b) by heating potassium borofluoride with potassium or magnesium, in a covered crucible :

$$B_2O_3 + 3Mg = 3MgO + 2B \; ; \quad 3K + KBF_4 = 4KF + B.$$

The reaction product is washed with hot hydrochloric acid, then with hot water and finally dried in a steam oven, when the amorphous form is obtained as a brown powder.

Hard, steel-grey boron is made by melting the amorphous boron in an electric arc in an atmosphere of hydrogen.

Pure crystalline boron is obtained as a black, hard solid by striking an electric arc between water-cooled copper electrodes in a mixture of boron trichloride vapour and hydrogen. $2BCl_3 + 3H_2 = 2B + 6HCl.$

Pure crystals of boron deposit on a tantalum filament heated to 1200° in a mixture of hydrogen and boron tribromide vapour.

The so-called crystalline boron (adamantine boron) made by fusing amorphous boron with aluminium and then dissolving out the latter with hydrochloric acid, is nothing but aluminium boride.

Properties.—(i) Boron is hard, steel-grey, high-melting-point solid ; it is unaffected by air or oxygen at ordinary temperature.

Crystalline boron is much harder but less reactive than the amorphous form—the former, for example, may be strongly heated in air without being oxidised, whereas the latter smoulders in air at 700°, forming B_2O_3 and some BN. The amorphous boron burns when heated in air, forming oxide and nitride.

(ii) It forms boron nitride when heated in a current of nitrogen ; boron nitride is decomposed by steam.

$$2B + N_2 = 2BN \; ; \quad BN + 3HOH = NH_3 + H_3BO_3.$$

(iii) It dissolves in oxidising acids, such as nitric acid or concentrated sulphuric acid, yielding boric acid, but it is not attacked by hydrochloric acid. $2B + 3H_2SO_4 = 2H_3BO_3 + 3SO_2$.

(iv) It reacts with fused alkalis to form borates and hydrogen.

$$2B + 2NaOH + 2H_2O = 2NaBO_2 + 3H_2.$$

(v) It forms boron trichloride when heated in chlorine ; boron trichloride may also be obtained by heating boron trioxide and coke together in a current of chlorine ; it is hydrolysed by water, yielding boric acid.

$$B_2O_3+3C+3Cl_2 = 2BCl_3+3CO \; ; \quad BCl_3+3HOH = 3HCl + H_3BO_3$$

Boron trifluoride is obtained by the spontaneous combustion of boron in fluorine or by heating a mixture of boron trioxide, fluorspar and strong sulphuric acid in a lead retort. $B_2O_3 + 3CaF_2 + 3H_2SO_4 = 2BF_3 + 3CaSO_4 + 3H_2O$.

It is decomposed by water yielding boric acid and fluoboric acid.

$$4BF_3 + 3HOH = H_3BO_3 + 3HBF_4.$$

(vi) Several *hydrides of boron*, such as boro-ethane B_2H_6 and boro-butane B_4H_{10}, have been prepared by the action of dilute hydrochloric acid upon magnesium boride. They are readily hydrolysed by water, yielding hydrogen and boric acid.

$$B_2H_6 + 6H_2O = 6H_2 + 2H_3BO_3.$$

(vii) Boron combines with most metals at high temperatures in the electric furnace, forming very hard *metallic borides*. Extremely hard boron carbide (hardest substance known) B_4C, an abrasive, is made technically by heating B_2O_3 and coke in an electric furnace.

$$3Mg + 2B = Mg_3B_2 \; ; \quad 2B_2O_3 + 7C = B_4C + 6CO.$$

(viii) Boron can displace carbon and silicon from their oxides on strong heating :

$$3SiO_2 + 4B = 2B_2O_3 + 3Si.$$

Boric Acid, H_3BO_3, also called **boracic acid,** is found in the *saffioni* (steam jets of the volcanic vapours in Tuscany)—this on condensation and concentration yields boric acid. It is prepared by adding concentrated hydrochloric acid to a hot saturated solution of borax—pearly white, silky crystals of boric acid separate on cooling :

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3.$$

These are washed with cold water and recrystallised from hot water.

Boric acid is manufactured mainly from native calcium borate, called *colemanite*. Sulphur dioxide is passed through powdered colemanite, suspended in boiling water; calcium sulphite and boric acid are formed—the former dissolving in excess of sulphur dioxide forming calcium bisulphite and the boric acid crystallising out on cooling:

$$2CaO,3B_2O_3 + 2SO_2 + 9H_2O = 2CaSO_3 + 6H_3BO_3.$$
$$2CaSO_3 + 2H_2O + 2SO_2 = 2Ca(HSO_3)_2.$$

Properties.—(i) Ordinary boric acid or *orthoboric acid*, H_3BO_3, forms soft, silky, pearly white crystals which are greasy to the touch, sparingly soluble in cold water but more freely in hot—solubility, 3.7% at 12° and about 28% at 100°. Boric acid is volatile in steam.

(ii) A very weak acid (weaker than carbonic acid), it turns yellow turmeric paper brown, and litmus wine-red, and has no action upon methyl orange. Since it is a weak acid its salts are hydrolysed by water. Boric acid may be titrated with caustic soda *in presence of an excess of glycerine,* using phenolphthalein as indicator. It then acts as a monobasic acid. $H_3BO_3 + NaOH = NaBO_2 + 2H_2O$.

(iii) Orthoboric acid is decomposed by heat, yielding metaboric acid, HBO_2, at 100°, and pyroboric acid, $H_2B_4O_7$, at 140°: still stronger heating yields a glassy mass of boron trioxide:

$$H_3BO_3 - H_2O = HBO_2\ ;\ 4HBO_2 - H_2O = H_2B_4O_7.$$
$$H_2B_4O_7 - H_2O = 2B_2O_3\ ;\ B_2O_3 + 3H_2O = 2H_3BO_3.$$

Boron trioxide is *an amphoteric oxide*; with water it forms boric acid. Boric acid yields boron hydrogen sulphate $B(HSO_4)_3$, with sulphur trioxide, and boron phosphate BPO_4 with phosphoric acid, showing feebly basic property of boron trioxide.

Uses. (i) In medicine as an antiseptic as borated cotton, boracic powder and *boracic ointment* which contains the acid mixed with vaseline or lard. It is used in weak solution as an eye lotion. (ii) in the manufacture of glass and glaze, and (iii) in the preservation of food.

Borax, $Na_2B_4O_7$, $10H_2O$, is sodium pyroborate (tetraborate). It is prepared from:

(i) *colemanite* by boiling the finely powdered mineral with sodium carbonate solution; the insoluble calcium carbonate is filtered off—the filtrate on concentration yields crystals of borax. The sodium metaborate in the mother-liquor is converted into borax by passing in carbon dioxide through the solution—the second crop of crystals of borax separates out, leaving the sodium carbonate in the solution.

$$2CaO,3B_2O_3 + 2Na_2CO_3 = 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2.$$
$$4NaBO_2 + CO_2 = Na_2B_4O_7 + Na_2CO_3$$

(ii) boric acid by boiling with soda ash—the solution is crystallised to yield borax: $4H_3BO_3 + Na_2CO_3 = Na_2B_4O_7 + 6H_2O + CO_2$.

(iii) native borax, called *tincal,* found in almost dried up lakes in Northern India and in Searle's lake in California, containing about 55 p.c. borax, by recrystallisation, i.e., crude borax is dissolved in hot water and then cooled when pure borax deposits.

Properties.—(i) Ordinary borax $Na_2B_4O_7$, $10H_2O$ is monoclinic and crystallises below 62°; above this octahedral borax $Na_2B_4O_7$,

$5H_2O$ separates. Borax forms white efflorscent crystals which are soluble in water—*the solution is alkaline due to hydrolysis* :

$$Na_2B_4O_7 + 7H_2O \rightleftharpoons 2NaOH + 4H_3BO_3.$$

Boric acid is so weak that a solution of borax (like sodium carbonate) may be titrated against hydrochloric acid, using methyl orange indicator.

$$Na_2B_4O_7 + 5H_2O + 2HCl = 4H_3BO_3 + 2NaCl.$$

(ii) When heated borax loses water and swells into a white mass, which then fuses to a colourless transparent glass, the so-called 'borax bead'.

The borax bead can dissolve metallic oxides to form metaborates which in certain cases have characteristic colours ; cobalt metaborate, for example, is blue.

$$Na_2B_4O_7 + CoO = 2NaBO_2 + Co(BO_2)_2.$$

The formation of coloured metaborates by certain metals is used in 'borax bead test' in qualitative analysis—the colour depends on whether the test is carried out in the oxidising or reducing flame of the Bunsen burner :

Compounds of :	Colour of borax bead in :	
	(oxidising flame)	*(reducing flame)*
Chromium	Green	Green
Manganese	Amethyst	Colourless
Iron	Yellow (cold)	Bottle green
Cobalt	Deep blue	Deep blue
Nickel	Brownish (cold)	Grey
Copper	Green (hot) ; blue (cold)	Colourless or red

Uses of borax.—(i) In the manufacture of optical and hard glass, enamels, and glazes for pottery ; (ii) As an antiseptic in making medicinal soaps, and in the the preservation of food, as a flux in soldering, in stiffening candle-wicks, and in laundering to give a gloss on ironing, (iii) In borax bead test in qualitative analysis.

Tests of boric acid.—(i) *Cobalt nitrate test.*—A blue mass is obtained on heating a borate moistened with cobalt nitrate solution on charcoal in an oxidising flame.

(ii) A solution of borate on being acidified with hydrochloric acid, turns turmeric paper brown.

(iii) A borate made into a paste with concentrated sulphuric acid and ethyl alcohol, and set fire to, burns with a green-edged flame.

$$B(OH)_3 + 3C_2H_5OH \rightleftharpoons B(OC_2H_5)_3 + 3H_2O.$$

The vapour of ethyl borate $B(OC_2H_5)_3$ formed burns with the green-edged flame.

Silicon

Symbol Si. Atomic weight 28.09. Atomic number 14. Density 2.49 (crystalline), 2.35 (amorphous). M. pt. 1420°C. B. pt. 2600°C. Valency 4.

History and occurrence.—Gay-Lussac and Thenard in 1809 obtained silicon by passing the vapour of silicon fluoride over heated potassium.

Next to oxygen, silicon is the most abundant element in the earth's crust containing to the extent of 25% as compared with 50% oxygen. It occurs as silicon dioxide or silica in various forms, such as *quartz, sand, agate* and *flint.* Silica is the acidic constituent of silicate minerals such as *clay,* Al_2O_3, $2SiO_2$, $2H_2O$, and *felspur,* K_2O, Al_2O_3, $6SiO_2$ in igneous rocks.

Preparation.—Silicon exists in two forms *amorphous and crystalline* :

Amorphous silicon is made : (i) by strongly heating a mixture of dry silica and magnesium powder in a covered silica crucible—magnesium oxide and excess silica are removed from the resulting mass by successively washing with hydrochloric acid and hydrofluoric acid : $SiO_2 + 2Mg = Si + 2MgO$.

(ii) by passing the silicon tetrachloride vapour over heated sodium or potassium—the product is washed with water to remove the chloride.

$$SiCl_4 + 4K = Si + 4KCl.$$

Crystalline silicon is made at Niagara by heating a mixture of sand and crushed coke in an electric furnace : $SiO_2 + 2C = Si + 2CO$.

Crystalline silicon is also formed when amorphous silicon is crystallised out from its solution in molten aluminium, and hence the production of crystalline silicon when its compounds, such as silica and silicon tetrachloride, are reduced with aluminium.

$$3SiCl_4 + 4Al = 4AlCl_3 + 3Si \ ; \quad 3SiO_2 + 4Al = 2Al_2O_3 + 3Si.$$

Properties.—(i) Amorphous silicon is a *light brown powder,* while the crystalline silicon forms *yellow to brown octahedral crystals with metallic lustre*—both the varieties are fusible at the high temperature of an electric furnace.

(ii) It is a non-metal—its oxide being distinctly acidic in character; but it is metallic in many of its physical characteristics ; thus the crystalline silicon possesses *metallic lustre* and marked *metallic conductivity.*

(iii) Amorphous silicon burns vigorously when heated in oxygen, and slowly when heated in air. $Si + O_2 = SiO_2$. *But the crystalline silicon is not attacked by oxygen even when strongly heated* ; in other chemical properties it resembles amorphous silicon.

(iv) Insoluble in water, it slowly decomposes steam at red heat :

$$Si + 2H_2O = SiO_2 + 2H_2.$$

(iv) It *spontaneously* ignites in fluorine, forming the fluoride, SiF_4, and burns when heated in chlorine, yielding silicon tetrachloride, $SiCl_4$; these halides are decomposed by water :

$$SiCl_4 + 4HOH = 4HCl + Si(OH)_4 \text{ (orthosilicic acid).}$$

(iv) It is insoluble in any single acid but it is attacked by a mixture of nitric and hydrofluoric acids :

$$Si + 6HF = 2H_2 + H_2SiF_6 \text{ (hydroflousilicic acid).}$$

(vii) It dissolves in hot concentrated caustic alkalis or in fused sodium carbonate :

$$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2 \ ; \quad Si + Na_2CO_3 = Na_2SiO_3 + C.$$

(viii) A mixture of volatile hydrides of silicon, such as silico-methane, SiH_4, and silico-ethane, Si_2H_6, etc., are formed by the action of hydrochloric acid upon magnesium silicide in absence of air : $Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$.

The silicon hydrides are spontaneously inflammable in air.

(ix) It combines with metals at high temperatures, forming metallic silicides, e.g., Mg_2Si.

Uses of silicon.—(i) As a deoxidiser in making steel, and (ii) in the manufacture of alloys such as *silicon-bronze*, *manganese-silicon-bronze*, ferro-silicon, and acid-resisting silicon steel, such as *ironac*, *tantiron* and *duriron*.

Silica, silicon dioxide, SiO_2.—Silica occurs in three amorphous forms *opal*, *agate*, and *flint*, and in the crystalline state as *quartz*, *tridymite*, and *cristobalite*. Quartz in its turn exists in three forms, *amethyst*, *cat's eye*, and *sand*. Three crystalline forms with transition points are :

$$\text{Quartz} \xrightleftharpoons{870^\circ} \text{Tridymite} \xrightleftharpoons{1470^\circ} \text{Cristobalite} \xrightleftharpoons{1710^\circ} \text{Liquid}$$

Quartz is the only stable form below 870°.

Silica also occurs in vegetable and animal organisms. It is found in the straw of cereals and bamboo cane, and in sponges. *Kieselguhr* is the siliceous skeletons of extinct *diatoms*.

Pure silica.—Pure silica is white solid but ordinary sand is sometimes yellow or brownish due to the presence of *ferric oxide* which may be removed by washing with hydrochloric acid.

Pure amorphous silica may be made from sand or silicate mineral by fusing with excess sodium carbonate in a platinum crucible when sodium silicate is formed—the fused mass is extracted with boiling water ; the aqueous extract of sodium silicate on acidification with HCl yields a gelatinous precipitate of silicic acid, which is washed with water, dried, and ignited :

$$MgSiO_3 + Na_2CO_3 = MgCO_3 + Na_2SiO_3$$

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3 \; ; \quad H_2SiO_3 = H_2O + SiO_2.$$

It may also be prepared by passing silicon tetrachloride into water—the gelatinous mass of orthosilicic acid formed is washed with water, dried and ignited :

$$SiCl_4 + 4HOH = 4HCl + Si(OH)_4 \; ; \quad Si(OH)_4 = 2H_2O + SiO_2.$$

Properties.—(i) Silica is insoluble in water, and in all acids except hydrofluoric acid : $SiO_2 + 4HF = SiF_4 + 2H_2O$.

(ii) An acidic oxide, silica dissolves in alkalis, and in fused sodium carbonate, yielding silicates. $2NaOH + SiO_2 = Na_2SiO_3 + H_2O$.

(iii) An intimate mixture of silica and coke heated to whiteness in a current of chlorine yields the colourless volatile liquid silicon tetra-chloride, $SiCl_4$: $SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$.

(iv) All the varieties of silica soften below 1600° and fuse in the oxyhydrogen flame at about 1700°. They become plastic before fusion and may be worked and blown like glass or drawn into threads.

(v) Silica, being non-volatile, can displace volatile acid anhydrides from their salts at high temperatures : $Na_2SO_4 + SiO_2 = Na_2SiO_3 + SO_3$.

Detection of silica.—(i) **Microcosmic salt bead test.**—When heated in a bead of microcosmic salt in a platinum wire loop, most silicates and also silica do not dissolve in the bead but swim about as a white skeleton. (ii) Vapours of silicon tetrafluoride are evolved by carefully heating a mixture of silica, calcium fluoride and concentrated sulphuric acid in a lead crucible—a drop of water at the loop of a platinum wire held in the vapour is coated with a white gelatinous deposit of silicic acid :

$$SiO_2 + 4HF = SiF_4 + 2H_2O. \qquad 3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4.$$

Uses of silica.—Quartz (sp. gr. 2.648) or **rock crystal** occurs sometimes in transparent colourless crystals, but more frequently in opaque or coloured masses. Colourless quartz is used for spectacle lenses, since it is not easily scratched, and for lenses and prisms in optical apparatus because of *its transparency to infrared and ultraviolet light.* Coloured varieties of quartz, such as amethyst, and cat's eye are used as gems.

Sand is quartz which has been crushed during its movement by water. It is extensively used in making glass, glaze, porcelain, mortar, silica-bricks, etc., and as building material. *Sand stone* is used in making mill-stones. *Agate* finds use in making mortars and knife-edges.

Silica glass, (quartz glass), made by using sand or quartz in oxy-hydrogen flame, possesses many remarkable properties. They are : (i) a very low coefficient of expansion so that white-hot silica may be quenched in water without cracking. and consequently the use of silica glass in making apparatus subjected to variations of temperatures, (ii) infusibility, its softening point is about 1500°—ordinary glass softens above 500°, (iii) transparency to visible light, and also to infrared and ultra-violet radiations, and (iv) it is free from alkalis and very resistant to attack by acids, and hence its use in the construction of crucibles, condensers, etc. *Vitreosil* is a translucent variety of silica glass. 'Vycor' is low-expansion glass, essentially of silica.

Carborandum, is an important abrasive, and is manufactured by heating a mixture of sand and crushed coke with a little saw dust and common salt in an electric furnace to a temperature of 1500° to 2000°C. *This is silicon carbide* :

$$SiO_2 + 3C = SiC + 2CO.$$

Silica gel, SiO_2, nH_2O, is obtained as a white gelatinous mass by heating to 100° a mixture of sodium silicate and hydrochloric acid. It is used in removing sulphur compounds from petroleum, and in drying air blast in iron metallurgy. It is used as an adsorbent and drying agent. Platinised silica gel is a contact catalyst in making sulphuric acid.

The silicic acids and silicates.—The acidic anhydride silicon dioxide being insoluble in water, silicic acids are formed by indirect means. Two important silicic acids are (i) *metasilicic acid,* H_2SiO_3, made by the action of acid on a silicate : $Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3$, and (ii) *ortho-silicic acid,* H_4SiO_4, made by the hydrolysis of silicon tetra halide :

$$SiCl_4 + 4HOH = Si(OH)_4 + 4HCl.$$

Many important silicates occur in rock minerals : **Talc** (soap stone) $H_2Mg_3(SiO_3)_4$—used in medicine and face powders ; **Asbestos,** $Mg_3Ca(SiO_3)_4$—used as a heat-insulator in making fire-proof materials and in covering steam pipes, etc., and as a filtering medium for corrosive liquids. Alumino-silicates form important constituent of many rocks and minerals. **Felspur** (ortho clase) $KAlSi_3O_8$, used in glaze, pottery and porecelain. **Kaolin** (china clay, $H_2Al_2(SiO_4)_2,H_2O$—used in pottery and porcelain, as a filler in paper, in making ultramarine, and also in medicine. Common clay, is impure aluminium silicate, used in making earthenwares, bricks, etc. **Mica** (biotite), $KHMg_2Al_2(SiO_4)_3$ and **Mica** (muscovite) $KH_2Al_3(SiO_4)_3$—used as electrical insulators, and also for making stove windows and lamp chimneys. **Garnet,** $Ca_3Al_2(SiO_4)_3$—used in making sand paper. **Beryl** is $Be_3Al_2Si_6O_{18}$.

Many silicates, e.g., zinc silicate, zinc beryllium silicate and cadmium silicate, are used as a fluorescent coating on the inside wall of fluorescent tubes (containing inert gas such as argon, and mercury vapour at 3 mm pressure)—colours produced by these silicates being green, yellow-white and yellow-pink respectively.

Meta-silicic acid, H_2SiO_3, is obtained as a white gelatious mass containing varying proportions of water, by the action of acids upon a soluble silicate : $Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3$. It is a very weak acid.

Colloidal silicic acid is obtained by slowly adding a dilute solution of sodium silicate to cold dilute hydrochloric acid—silicic acid remains in solution in the colloidal state. It is purified by dialysis. It is known as silicic acid sol. (p. 148).

Sodium silicate, (soluble glass), Na_2SiO_3, is prepared by fusing white sand with nearly twice its weight of sodium carbonate in a reverberatory furnace. $Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$.

The resulting mass is dissolved in hot water under pressure in autoclaves to form a thick solution known as **water glass.** The solution is strongly alkaline due to hydrolysis.

Sodium silicate is used as an adhesive cement for joining pieces of china, as filler in cheap soaps, in solution as a preservative for eggs, as an adhesive in making carboard boxes, as a detergent in laundries, as a heat-resistant binding agent, to render bricks and cements non-porous. Potassium silicate, K_2SiO_3 is also soluble glass.

Solution of water glass gives a white gelatinous precipitate of silicic acid with ammonium chloride or ammonium carbonate solution :

$$Na_2SiO_3 + 2NH_4Cl + 2H_2O = H_2SiO_3 + 2NaCl + 2NH_4OH$$

It also gives a yellow precipitate of silver silicate, soluble in dilute acids and ammonia, with silver nitrate solution.

$$2AgNO_3 + Na_2SiO_3 = Ag_2SiO_3 + 2NaNO_3.$$

On placing crystals of soluble salts of such metals as copper, nickel, cobalt and manganese at the bottom of a glass trough filled with a solution of sodium silicate, sp. gr. 1.1, and keeping overnight, beautiful tree-like growths of insoluble silicates, known as *silica garden*, develop (fig. 154).

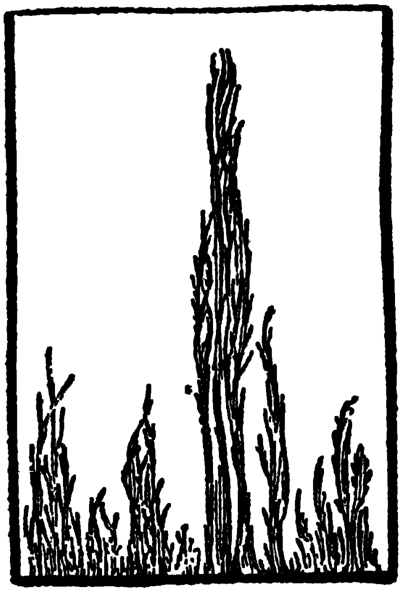


Fig. 154

Silicon tetrafluoride, SiF_4.—Silicon ignites spontaneously in fluorine, forming gaseous silicon tetrafluoride. It is usually prepared by heating a mixture of fluorspar, CaF_2, and white sand with concentrated sulphuric acid. The gas is passed over dry sodium fluoride to remove HF, and is collected over mercury.

$$2CaF_2+2H_2SO_4+SiO_2 = 2CaSO_4+SiF_4+2H_2O.$$

Silicon fluoride is a colourless strongly fuming gas. It is decomposed by water, forming gelatinous *ortho silicic acid*, $Si(OH)_4$, and hydrofluo-silicic acid H_2SiF_6,—*a fact utilised in testing silicates or fluorides.*

$$3SiF_4 + 4H_2O = Si(OH)_4 + 2H_2SiF_6.$$

Hydrofluosilicic acid, H_2SiF_6, is made in aqueous solution (the pure acid is not known) by passing SiF_4 in water. The gas, SiF_4, is prepared by heating a mixture of fluospar, fine white sand and concentrated sulphuric acid in a flask, and is passed into water contained in a cylinder—the end of the dry delivery tube dipping into a layer of mercury (a device that prevents the tube becoming choked with gelatinous silicic acid).

The silicic acid is filtered off. The filtrate is an aqueous solution of hydrofluosilici acid. It is partly decomposed in solution : $H_2SiF_6 \rightleftharpoons SiF_4 + 2HF$.

The fluosilicates, Na_2SiF_6 and K_2SiF_6, are insoluble and are precipitated by H_2SiF_6. Magnesium fluosilicate, $MgSiF_6$, solution is painted over concrete floor to harden and polish the surface. Na_2SiF_6 is used as an insecticide for chickens.

Glass.—Glass making is of great antiquity, and it was known to the ancient Hindus long before Christian era. But it is generally believed that the art originated in Egypt, where natural carbonate of soda occurs. In the period 2000—1500 B.C. an important glass industry developed in Egypt. From Egypt the knowledge spread to Rome, Constantinople and Venice. The rest of Europe learnt the art from Venice.

Glass was extensively employed by the Romans for domestic purposes, and in Britain it was produced during Roman occupation. Glass making was also developed very early in Assyria. In modern times the most advanced processes of glass manufacture were carried on mostly at Jena in Germany.

Definition.—*Glass is an amorphous transparent mass of a complex mixture of the silicates of one or more alkali metals with the silicates of one or more heavy or alkaline earth metals, which is produced when a liquid melt solidifies without undergoing crystallisation.*

Glass is an apparently solid substance, since it has no sharp melting point ; when heated, it gradually softens and finally liquefies, and hence it is considered as a viscous liquid that has been supercooled.

Glass is completely *isotropic*, i.e., it exhibits simliar properties in all directions. Glass has the valuable property of becoming *plastic* on heating, when it can be blown, moulded or rolled into sheets ; molten glass gradually solidifies on cooling *without showing any tendency to crystallisation.* Glasswares, however, develop, usually after a lapse of many years, a tendency of losing its transparency and becoming opaque due to the crystallisation of the component silicates. This is known as *devitrification of glass.* Glass also devitrifies when heated long to its softening point. *A bad conductor of heat,* glass wares generally crack, when subjected to sudden changes of temperature. Glass is more or less resistant to the attack by all chemical reagents *except hydrofluoric acid*—alkalis, however, have very slow corroding action upon glass.

The Composition of glass.—As already stated, glass is a complex mixture of several silicates ; *all glass contains silica.* Common soda glass contains sodium and calcium silicates, and has the approximate composition Na_2O, CaO, $5SiO_2$. In addition to or in place of soda, Na_2O, and lime, CaO, special glasses may contain potash, K_2O, baryta, BaO, magnesia, MgO, lead oxide, PbO, and zinc oxide, ZnO, etc. ; they may also sometimes contain *borates* and *phosphates.* The properties of glass are profoundly modified by its composition, and hence based on its composition, glass has been broadly classified into :

(i) **Soft glass** or **soda glass** : it contains sodium and calcium silicates, and is easily fusible ; e.g., common laboratory glass, window glass, and plate glass.

(ii) **Hard glass (potash** or **Bohemian glass)** : it contains potassium and calcium silicates, and is harder, less easily fusible, and more resistant to the attack of chemical reagents ; hence its use in making chemical apparatus and combustion tubes, etc. Potash is employed as potassium carbonate.

(iii) **Flint glass** : it contains potassium and lead silicates, and has high density and refractive index ; hence its use in making lenses and prisms. Flint glass is very soft. Lead is used in the form of litharge, PbO, or red lead, Pb_3O_4.

(iv) **Optical glass** : it contains as acidic oxide boron trioxide and phosphorus pentoxide in place of some silica, and barium oxide instead of lime, and occasionally some zinc oxide. Two main types of an optical glass are : *Crown glass* which contains as basic oxide mainly potash and barium oxide, and *flint glass* in which litharge replaces lime.

(v) **Jena glass** and **Pyrex glass** : they are highly resistant to the action of heat and chemical reagents.

Jena glass contains zinc and barium oxides, and boron trioxide in place of some silica ; it is mainly a mixture of zinc and barium boro-silicates. It is low in alkali content but rich in alumina compared to ordinary glass. *Pyrex glass* contains boron trioxide and is very rich in silica, but poor in alkali and alumina. It contains sodium and aluminium boro-silicates.

It may be noted that (i) increase of silica content, renders glass less fusible and harder, but more brittle, (ii) lime reduces fusibility, also increases hardness but does not increase brittleness (iii) alkali makes glass softer, more fusible and less resistant to chemicals. Ordinary glass absorbs heat radiations and hence its use in fire-screens.

Manufacture of Glass.—Common soda glass contains calcium and sodium silicates, and has the approximate composition Na_2O, CaO, $5SiO_2$. It is made by fusing together : (i) *silica* used in the form of white sand (free from iron compounds), or crushed quartz, (ii) *alkali* employed as soda-ash or in the form of a mixture of saltcake and charcoal, when sulphur dioxide is evolved :

$$2Na_2SO_4 + C + 2SiO_2 = 2Na_2SiO_3 + CO_2 + 2SO_2$$

and (iii) *lime*—chalk or limestone or lime itself is used. A typical 'charge' for making a batch of common glass consists of 100 parts of sand, 35—40 parts of soda-ash, 15 parts of limestone, to which is added varying amount of *cullet* (broken glass). The addition of cullet helps the fusion of the charge. The raw materials are separately crushed, and freed from impurities like iron which imparts colour to the glass. The batch of different raw materials is gradually introduced into a fireclay *tank furnace* (fig. 155) heated by producer gas and air on the regenerative principle of heat economy to a temperature of about 1400°C, until it is almost filled with the molten material. The charge fuses, with evolution of gases, into a mobile liquid which is stirred by a fireclay rod to obtain a homogeneous melt.

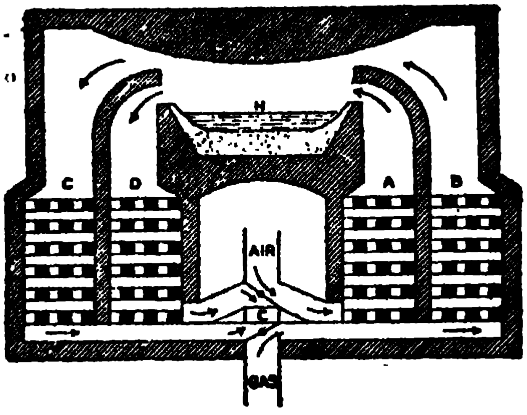


Fig. 155

Decolourising agents, such as manganese dioxide, nitre, etc. are then added to the molten glass to neutralise the green tint of *ferrous iron*, generally present in the raw materials,—iron being thereby oxidised into the ferric state imparts a faint yellow colour which is complimentary to the pink colour of manganese silicate, the product is colourless glass. When the charge has assumed a state of quiet fusion, and is free from all bubbles of gas, the molten glass is gradually cooled to a pasty mass which is then worked into different wares either by blowing or by casting in moulds or made into sheets (plate glass) by pressing between rollers.

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2 \; ; \quad CaCO_3 + SiO_2 = CaSiO_3 + CO_2.$$

Annealing of glass.—All varieties of glass prepared as above require *annealing* before use, since they are liable to crack on heating owing to the existence of internal strain in them. The defect is remedied by heating the glass wares to a temperature of about 500°C so as not to get deformed and then slowly and uniformly cooling by passing through a tunnel-like furnace: the process is known as annealing.

Coloured glass is made by adding various metallic oxides or other substances to the molten glass in course of its manufacture.

Colour of glass	Colouring agent	Colour of glass	Colouring agent
Ruby red	Gold, selenium, cuprous oxide.	Green	Chromic oxide, ferric oxide with a reducing agent.
Blue	Cobalt oxide, cupric oxide.	Amber	Carbonaceous material with sulphur or iron sulphide.
Opal	Fluorspar with felspar; tin dioxide or calcium phosphate.	Violet	Manganese dioxide.
Yellow	Cadmium sulphide, uranium oxide.	Black	Excess of pyrolusite and ferric oxide.

Coloured glasses are generally made by melting the batch in clay pots. Artificial gems are often coloured glasses only.

Safety glass, used in automobiles, consists of a (polyvinyl acetate resin) plastic sheet sandwiched between two pieces of thin plate glass—it may be shot through by a bullet without shattering. Tempered plate glass is also often used as safety glass.

Fibre glass is glass reduced to flexible filaments or threads. It is an excellent heat insulator. Fibre glass is woven into fabrics for fireproof curtains. It is also used as a packing material for distillation columns. Glass is also spun into short fibres, known as *glass wool.*

Composition :	SiO_2	Na_2O	K_2O	CaO	PbO	Al_2O_3	ZnO	B_2O_3
Sodalime glass	76	13		11				
Potash ,,	71		18	11				
Flint ,,	53		14		33			
Jena ,,	65	8				5	12	10
Pyrex ,,	81	5				2		12

When the common glass is manufactured from impure (containing iron oxide) raw materials, it generally assumes a green and yellow colour, and is known as **bottle glass.** It contains sodium, calcium and iron silicates. It is used in making cheap medical phials, and bottles, etc. *Common glass is found to contain a trace of free alkali.*

Enamel is ordinary glass rendered opaque by opacifiers like tin dioxide, antimony oxide, and barium sulphate. Enamelling of iron or brass wares prevents atmospheric corrosion, and hence the use of enamelled name plates, and sign boards, etc.

Pottery and porcelain.—The manufacture of china or porcelain was discovered in China in the seventh or ninth century A.D. The basis of pottery and porcelain is *china clay* or *kaolin*, Al_2O_3, $2SiO_2$, $2H_2O$, which is easily moulded when wet and retaining its shape on drying and firing. *Porcelain* is made from a mixture of pure clay and finely-ground felspar and quartz—the plastic mass is worked on a potter's wheel, dried in hot chambers, and then burnt in fire-clay boxes called *seggars*, stacked in a kiln ; the ceramic body after firing is called *biscuit*. Earthen were is similarly made from clay only. The body after firing is porous and requires glazing. The *glaze* is easily fusible glass imparted to the surface of the porous body, and having the same composition as the clay beneath. Porcelain is glazed by dipping into a creamy paste of a mixture of ground felspar, quartz, kaolin, and firmly adheres to the surface. Table ware is usually glazed with a mixture of lead oxide, clay and flints. Earthenware drain-pipes are salt-glazed by throwing common salt into the kiln.

Besides its use in making china, kaolin is employed as a filler in paper and textile industries. Clay is also made into bricks and tiles. Clay containing a high proportion of silica and alumina is very refractory, and is called **fireclay.** It is used in making **firebricks.**

Fuller's earth is non-plastic clay used for decolorising oils, etc. Clay is often contaminated with lime-stone, sand and iron oxide ; *marl* is a mixture of clay and limestone.

Comparison of carbon, silicon, and boron.—In many of its properties carbon resembles silicon with which it belongs to the fourth group in periodic table. In spite of their belonging to two different groups B and Si show similarities owing to *diagonal relationship* in periodic table.

Properties	*Carbon*	*Silicon*	*Boron*
Allotropy	High-melting non-metals, all these elements exist in two allotropic forms, amorphous and. crystalline. Graphitic carbon and crystalline silicon possess metallic lustre and electrical conductivity.		
Melting point	3500°	1420°	2300°
Density	2.25 graphite 3.5 diamond	2.5 crystalline 2.35 amorphous	2.34
Action of oxygen	Burns to CO_2	Amorphous form burns to SiO_2	Burns in air to B_2O_3 and BN.
Action of Acids	Graphite is oxidised by HNO_3 and $KClO_3$ to graphitic acid.	Dissolves in a mixture of HF and HNO_3	Dissolves in oxidising acids HNO_3 and H_2SO_4.
Action of steam	Charcoal decomposes steam at red heat.	Slowly decomposes steam at red heat.	—
Action of alkali	—	Dissolves with liberation of H_2	Reacts with liberation of H_2.
Oxides	CO_2 gas, fairly soluble in water, *feebly acidic* ; forms carbonic acid and carbonate. CO, gas.	SiO_2, solid, insoluble, feebly acidic, anhydride of silicic acid, forms silicate. SiO, solid.	B_2O_3, glassy solid, amphoteric, forms boric acid with water and boron-phosphate with phosphoric acid.
Fluroide and chloride.	CF_4, inert gas and CCl_4, inert liquid—both are stable towards water.	SiF_4, gas and $SiCl_4$, liquid—both are hydrolysed by water.	BF_3 gas and BCl_3, liquid, b.p. 12.5—both are hydrolysed by water.
Hydrides	CH_4, C_2H_6, etc. are inert gases, not attacked by alkali.	SiH_4 gas, and Si_2H_6 liquid—spontaneously inflammable and attacked by alkali.	B_2H_6, etc. decomposed by water.
Sulphides	CS_2 inflammable liquid.	SiS_2 inert solid.	B_2S_3 solid—hydrolysed by water.
Metallic compounds.	Carbides CaC_2, etc	Silicides $CaSi_2$, etc.	Borides Mg_3B_2,etc.

Exercises

1. What is borax? How is it obtained on a large scale? Of what use is this compound in qualitative analysis? How may (a) boric acid, (b) boron trichloride, (c) boron, and (d) boric oxide, be obtained from borax? *Calcutta* '44.

2. Describe the preparation and properties of silicon, and discuss its relationship to boron and carbon, by considering the properties of the elements and their compounds.

3. Give methods for the preparation of boric acid. Give one method for the detection of boric acid or a borate. Explain the chemistry of borax bead test in qualitative analysis. *Bombay* 1953.

4. What do you know about the occurrence, properties and uses of silica? What happens when (a) silica is strongly heated with carbon, (b) chlorine is passed over a heated mixture of coke and silica? Starting from sand how would you prepare specimens of (i) water-glass, (ii) silicon tetrafluoride, and (iii) silica gel? *Allahabad Inter.*

5. What is glass? How is it manufactured? Give an account of the different varieties of glass. What are transparent silica and ruby glass? *U. P. Board* '41.

6. How does silica occur in nature? What are its uses? How would you prepare silicon from silica? Write what you know about the allotropic modifications of silica. *Calcutta* '55.

7. What is dialysis? Describe an experiment to illustrate it. How will you prepare colloidal silicic acid and silica from sodium silicate? (p. 148).

XXVI

METALS AND METALLIC COMPOUNDS

Metals are in the service of man from prehistoric days. Our material civilisation has been largely due to our knowledge and application of metals. The 'bronze age', in human history followed the 'stone age' and preceded the present 'age of steel'. About seventy-four of the elements are metals.

Metals are generally found in nature as natural materials, called **minerals,** usually in the form of oxides (e.g., hæmatite, cassiterite, and bauxite, etc.), sulphides (e.g., zinc blende, galena, cinnaber, and copper pyrites, etc.), carbonates (e.g., lime-stone, magnesite, and dolomite, etc.), and silicate (e.g., felspar, mica, and kaolin, etc.), etc. A few metals, such as copper, gold and platinum, are sometimes found as such in nature, and are then said to occur *native.*

Metallurgy: *The winning and refining of metals.*—Metals are obtained from ores. **An ore** is a mineral that may be profitably and conveniently treated for the extraction of one or more metals. Metallurgy is the science and art of winning (or extracting) a metal from its ore.

Every metallic mineral is not suitable for the winning of the metal; iron pyrites, for example, is not suitable for the smelting of iron, and is not, therefore, an 'ore' of iron.

The method of winning metals from ores varies with the particular metal and the nature of the ores. Native copper, gold and platinum are worked up by refining only.

Important processes for the extraction of metals include:

(i) **The carbon-reduction process.**— The process involves the reduction of a compound of the metal, the ore, to the free metal. The principal reducing agent is carbon, usually in the form of coke. A typical procedure for the treatment of ores, consists of the following operations: (a) *crushing* and *grinding,* (b) *concentration,* (c) *calcination* or *roasting,* (d) *smelting* or *reduction.*

(a) **Crushing and grinding.**— The ore, usually found as a rock mass, is first crushed to pieces,—a *stone-breaker, jaw crusher, grinding mill* or *stamps* being employed according to the degree of fineness required. The broken staff is then separated into sizes by a series of screens.

(b) **Concentration of the ore,** also called **dressing the ores.** The ore generally contains rocky impurity, such as silica and silicates called **gangue** or **matrix.** Hence the necessity of dressing the ores before calcination and smelting. One or more of the following operations are usually employed.

(1) **Gravity separation.**— The crushed ore is washed in a current of water which carries away the light sileceous gangue, leaving the heavy ore behind; the process is used in concentrating the tin ore, cassiterite.

(2) **Magnetic separation.**—Many ores differ in magnetic property from rocky impurity; magnetic wolfram is removed from non-magnetic cassiterite by electromagnetic separation.

(3) **Oil-floatation process.**— The process works particularly well with *the sulphide ores,* and is used in concentrating copper pyrites, galena, and blende. The crushed ore is churned up with water containing a little oil, such as pine and eucalyptus oils, which wets the ore but not the gangue—the ore therefore, collects in the froth formed on the surface of the liquid, and is removed; the gangue is wetted by water and consequently sinks to the bottom. The ore is separated from the froth. Thus the *ore concentrate* is obtained.

(c) **Calcination and roasting.**— *Roasting* is a process of heating the ore *without fusion in a plentiful supply of air* in order to *oxidise* it. *Calcination* means heating the ore in air without fusion, the purpose being to drive off moisture and volatile matter from the ore. But the two terms are often used in the same sense; roasting, however, usually involves higher temperature than calcination. Moisture, carbon dioxide and impurities, such as arsenic, which form volatile oxides, are eliminated during calcination. The calcined material is in a *porous state,* and is therefore readily reduced duriang smelting.

The ore concentrates are, usually, subjected to calcination; the oxide minerals cassiterite and hæmatite, for example, are calcined. The carbonate minerals, such as magnesite, $MgCO_3$, and *siderite,* $FeCO_3$, are calcined to their oxides:

$$MgCO_3 = MgO + CO_2; \quad FeCO_3 = FeO + CO_2.$$

Ferrous oxide is converted to the ferric state during calcination.

The *sulphide minerals, such as blende* and *galena,* are roasted in air and *sintered* with incipient fusion at high temperatures in order to convert them to oxides:

$$2ZnS + 3O_2 = 2ZnO + 2SO_2; \quad 2PbS + 3O_2 = 2PbO + 2SO_2.$$

(d) **Smelting or reduction.**— The calcined ore containing metallic oxide, mixed with carbon and flux, is smelted in a furnace, when the oxide is reduced to the metal—*smelting* is an operation whereby the metal is separated *by fusion* from the ore.

(A **flux** is a substance added to the furnace charge to remove the gangue forming a fusible body, called a *slag* or *cinder*;)

flux + gangue = slag

The selection of flux depends upon the nature of the gangue; it must be acid to remove basic impurities, and basic for acid impurities. In the smelting of iron the acid gangue silica is fluxed with lime, yielding a slag of calcium silicate, while in the extraction of copper ferrous oxide is removed as a slag of ferrous silicate by adding the acid flux silica. The molten slag floats on the surface of liquid metal (and hence protects it from the action of air), forming an immiscible layer which can be easily drawn off.

The metals below aluminium in the electro-chemical series (p. 130) are usually obtained by the reduction of their oxides with carbon; e.g., *zinc, iron, tin, lead,* and *copper.* The oxides of aluminium and metals above it in the series (*except magnesium*) are too stable to be reduced by carbon; these metals are therefore, obtained by electrolytic methods. Magnesium oxide is reduced by carbon at the high temperature of electric furnace.

Furnaces.— A furnace is simply a heating device designed for the production, control, and continuous application of heat. It is electrically heated (*electric furnace*) or fired by fuels (combustion furnaces)—fuels may be solid (coal), liquid (petroleum oil) or gaseous (producer gas, coke oven gas, etc.). Various types of furnaces are used in metallurgy—common types are: (i) **Kiln** in which fuel and material are mixed and air is freely admitted but no fusion takes place, e.g., lime kiln. (ii) **Blast furnace** in which fuel and material are mixed and air-blast is sent in near the bottom and fusion of the charge occurs, e.g., metallurgy of iron, copper, and lead, (iii) **Reverberatory furnace** in which the fuel is burnt in a separate part of the furnace, called the *fire-place* or *grating*—the flame and hot gases only coming in contact with the material heated. The furnace (fig. 156), is used when it is desired to heat the charge without mixing with the fuel. The chief feature of the furnace is that the flames from the fire place strike against the arched roof of the furnace and are deflected on to the charge on the *hearth.* Reverberatory furnace is used both for roasting and smelting.

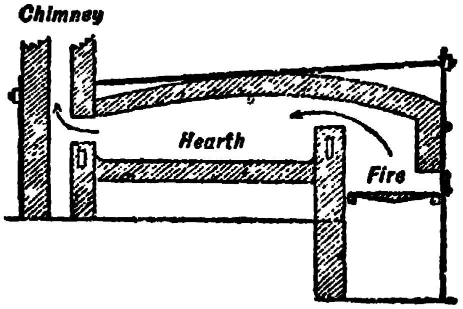


Fig. 156

(iv) **Muffle furnace** in which the chamber (called muffle) containing the material is heated externally by the flame and fire gases circulating in flues surrounding it. Products of combustion as well as the fuel do not come in contact with the material in a muffle furnace, e.g., salt-cake muffle furnace. Electric muffles are also frequently used. (v) **Retort furnace** is heated externally, e.g., metallurgy of zinc. (vi) **Regenerative furnace** in which the sensible heat of the escaping gases from the furnace is used to preheat the air or air and gas, supplied to furnace, e.g., open hearth furnace for making steel, tank furnace for glass.

Electric furnaces (arc—, resistance—, or induction furnaces) are largely used when high temperatures (manufacture of calcium carbide, graphite, etc.) or electrolytic reduction (extraction of Al) are required, and where eletric power is cheap, e.g., hydroelectric power. An electric furnace is capable of producing as a high a temperature as 4000°C whereas the highest in a combustion furnace is somewhat below 1500°.

(ii) **The self-reduction process.**— As already stated above, the sulphide ores are roasted and sintered into oxides, which are then smelted with carbon, e.g., zinc blende and galena. But it is often *partially* roasted, and the oxide or sulphate produced is reduced by the unchanged sulphide during smelting. This is a *self-reduction process,* since the reduction takes place by the sulphide itself:

$$2PbS+3O_2 = 2PbO+2SO_2 ; \quad PbS+2O_2 = PbSO_4$$

$$2PbO+PbS = 3Pb+SO_2 ; \quad PbS+PbSO_4 = 2Pb+2SO_2$$

Copper and lead are made by the self-reduction process.

The metals, of which the oxides readily lose oxygen, can be obtained by simple roasting or by smelting with lime :

$$HgS + O_2 = Hg + SO_2 ; \quad 4HgS + 4CaO = 4Hg + 3CaS + CaSO_4.$$

Sulphide minerals can be reduced by iron, which is converted into iron sulphide : $Sb_2S_3 + 3Fe = 2Sb + 3FeS$; $HgS + Fe = Hg + FeS$.

(iii) **The thermit process.**— Some metals, e.g., Cr and Mn, are made by reduction of their oxides with a more active metal, e.g., aluminium.

$$Cr_2O_3+2Al = 2Cr+Al_2O_3 ; \quad 3Mn_3O_4+8Al = 9Mn+4Al_2O_3.$$

(iv) **The electrolytic method.**— The alkali and alkaline earth metals are too strongly electro-positive (standing at the head of the electrochemical series) to be made by the electrolysis of the aqueous solutions of their salts ; they are obtained by the electrolysis of *fused chlorides* ; e.g., *sodium, potassium, calcium,* and *magnesium.* Fused hydroxide is also used for sodium and potassium.

Aluminium is also too electro-positive to be separated from its aqueous solution. It is made by the electrolysis of aluminium oxide dissolved in a bath of molten cryolite and fluorspar.

Metals below aluminium in the series may also be isolated by the electrolysis of an aqueous solution. The process is used for obtaining copper and zinc (*wet process of metallurgy*). The electrolytic method is generally applied for the refining of metals ; e.g., *copper, nickel, tin* and *lead.*

(v) **Special process.**—Gold and silver are extracted by *amalgamation with mercury*—the mercury is subsequently distilled off. The metals may also be obtained by *alloying with lead* and then removing the lead by *cupellation.*

Processes involving precipitation of the noble metals gold and silver from aqueous solutions are in use ; e.g., in the *cyanide process* gold and silver are precipitated from the cyanide leach by scrap zinc. Copper is precipitated from aqueous solution by scrap iron : $CuSO_4 + Fe = FeSO_4 + Cu$.

Refining of metals.— The crude metals obtained by smelting, are generally *thermally refined* : (i) by the *oxidation* of the easily oxidisable impurities by passing air through the molten metal : e.g., *copper, iron,* and *tin,* etc. ; (ii) by the *distillation* of easily volatile metal ; e.g., *zinc,* etc. ; (iii) by the *liquation* of readily fusible metals, e.g., *tin,* etc.

Chemically pure metal is however made by electrolytic refining ; *Copper, aluminium, silver,* and *lead* etc.

Usual methods for winning a metal from its sulphide ore are : (a) simple roasting in air, e.g., mercury, or roasting in air to oxides and then reduction with carbon, e.g., zinc and lead, (b) self-reduction process, e.g., copper and lead, (c) reduction with iron, e.g., mercury and antimony, (d) electrolytic process, e.g., zinc and copper. Silver is obtained from silver glance, Ag_2S, by the cyanide process.

Alloys.— An alloy is a metallic material containing two or more elements in intimate association, usually produced on solidification of the molten mixture. The principal objects of alloy-making are : (i) to improve—the mechanical properties, such as hardness, tensile strength, etc., (ii) to facilitate the production of sound and workable castings and (iii) to resist the atmospheric and chemical corrosion. Alloying generally decreases the malleability and conductivity of metals.

Alloys are made : (i) by fusing the metals together or mixing them in the molten state—this is the method commonly used. Brass is made by melting zinc and copper together; (ii) by compression of finely divided metals; Wood's fusible alloy is thus prepared from Pb, Sn, Bi and Cd powders; (iii) by simultaneous electrodeposition of metals from a solution, e.g., copper and zinc as brass, from a solution of their cyanides in potassium cyanide.

The solid alloy may either be homogeneous or heterogeneous; a homogeneous alloy may be *solid solution, a pure compound* or *a solid solution of a compound in excess of one of the metals.* The separate phases of a heterogeneous alloy may consist of *pure metals*, one or more *compounds*, or *solid solutions* of metals or their compounds, in metals.

An amalgam is an alloy containing mercury as one of the components, e.g., sodium amalgam.

Alloys find extensive applications in arts and industries. Modern machine civilisation depends not a little upon the proper fabrication of alloys. Several useful alloys are :

Alloy	Composition in per cent	Uses
Brass	Cu 60-80, Zn 40-20	Sheets, tubes, etc.
Bronze	Cu 75-90, Sn 25-10	Coins, statues, etc.
Stainless steel	Fe 88-86, Cr 12-14	Cutlery.
Magnalium	Al 98, Mg 2	Airship construction.
Duralumin	Al 95, Cu 4, Mg 0·5, Mn 0·5	Airship construction.
German silver	Cu 25-50, Zn 35-25, Ni 35-10	Plates, etc.

Metallic compounds.—Oxides : Oxides may be prepared:

(i) by heating a metal in air or oxygen, except the noble metals gold, silver and platinum ; e.g., $2Zn+O_2=2ZnO$.

(ii) by passing steam over a red-hot metal ; e.g.

$$Mg+H_2O = MgO+H_2 ; \quad 3Fe+4H_2O = Fe_3O_4+4H_2.$$

(iii) by heating the hydroxide, carbonate, and nitrate of a metal (except sodium and potassium) or by roasting the sulphide in air.

$$2Al(OH)_3 = Al_2O_3+3H_2O ; \quad CaCO_3 = CaO+CO_2$$

$$2Pb(NO_3)_2 = 2PbO+4NO_2+O_2 ; \quad 2ZnS+3O_2 = 2ZnO+2SO_2$$

(iv) by precipitating unstable hydroxides, such as of mercury and silver, by caustic soda solution:

$$2AgNO_3+2NaOH = 2NaNO_3+Ag_2O+H_2O.$$

Properties:— (i) The oxides are insoluble in water, except those of alkali and alkaline earth oxides which dissolve yielding hydroxides—magnesium oxide is only slightly soluble : $Na_2O + H_2O = 2NaOH$; $CaO + H_2O = Ca(OH)_2$.

(ii) The oxides, being basic, dissolve in acids, yielding salt and water; the amphoteric oxides of zinc, tin, lead and aluminium, react both with acids and alkalis ; $ZnO + 2HCl = ZnCl_2 + H_2O$; $ZnO + 2NaOH = Na_2ZnO_2 + H_2O$.

(iii) Peroxides dissolve in dilute acids, yielding hydrogen peroxide; polyoxides, e.g., of lead and manganese, dissolve in hot concentrated H_2SO_4 and HCl, yielding oxygen and chlorine respectively :

$$2PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O + O_2.$$
$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2.$$

Hydroxides.—Preparation : Soluble hydroxides of alkali and alkaline earth metals may be made by dissolving the metal or oxide in water. $CaO + H_2O = Ca(OH)_2$; $2Na + 2H_2O = 2NaOH + H_2$.

(ii) Insoluble hydroxides are precipitated by the action of caustic soda or ammonium hydroxide upon a salt solution. Caustic soda is the precipitant used, if the hydroxide is soluble in ammonia or ammonium salts, e.g., *hydroxide of copper.* Ammonium hydroxide is employed in precipitating amphoteric hydroxides, which are soluble in caustic soda ; e.g., *hydroxides of zinc, aluminium* and *tin.* Hydroxides of *silver and mercury* being unstable, caustic soda precipitates their oxides: $Al_2(SO_4)_3 + 6NH_4OH = 3(NH_4)_2SO_4 + 2Al(OH)_3$.

$$MgCl_2 + 2NaOH = Mg(OH)_2 + 2NaCl.$$

Properties.—(i) Sodium and potassium hydroxides are white crystalline deliquescent solids which are *highly corrosive;* other hydroxides are also white, except the *pale blue* copper hydroxide and the brown ferric hydroxide.

(ii) Sodium and potassium hydroxides are *soluble in water*—solution strongly alkaline (*caustic alkalis*); other hydroxides are insoluble, except $Ca(OH)_2$ which dissolves fairly in water; $Mg(OH)_2$ is only slightly soluble.

(iii) The hydroxides, being all *basic,* dissolve in acids, yielding salt and water. The amphoteric hydroxides of Zn, Al, Sn and Pb, also dissolve in caustic soda or potash; hydroxides of Ca, Mg and Zn are soluble in excess of ammonium salts. Copper hydroxide dissolves in excess of ammonia, giving a *deep blue* solution. $2Al(OH)_3 + 2NaOH = 2NaAlO_2 + 4H_2O$.

$$Mg(OH)_2 + 2NH_4Cl = MgCl_2 + 2NH_4OH.$$

(iv) Sodium and potassium hydroxides *melt* without decomposition, on heating; other hydroxides are decomposed by heat into oxide and water :

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

(v) Sodium and potassium hydroxides precipitate insoluble hydroxides of metals from salt solutions, and liberate ammonia from ammonium salts—calcium hydroxide does also liberate ammonia from its salts :

$$NH_4Cl + NaOH = NH_3 + H_2O + NaCl.$$

Chlorides.—Preparation.- (i) *Anhydrous chlorides* are generally prepared: (i) by heating the metal in a current of chlorine or hydrochloric acid gas, e.g., $Sn + 2Cl_2 = SnCl_4$: $Sn + 2HCl = SnCl_2 + H_2$.

(ii) by heating a mixture of metallic oxide and coke in a current of chlorine, e.g., $MgO + C + Cl_2 = MgCl_2 + CO$.

or (iii) by heating a hydrated chloride in a current of HCl gas, e.g., anhydrous $MgCl_2$.

(b) *Hydrated chlorides* are made: (i) by dissolving the metal in hydrochloric acid or aqua regia:

$$Fe + 2HCl = FeCl_2 + H_2;\quad Fe + 3Cl\ (\text{aqua regia}) = FeCl_3.$$

Pb, Cu, Hg and Ag do not dissolve in hydrochloric acid.

or (ii) by dissolving the oxide, hydroxide, carbonate or sulphide of the metal in hydrochloric acid, e.g.,

$$Fe_2O_3+6HCl = 2FeCl_3+3H_2O; \quad Al(OH)_3+3HCl = AlCl_3+3H_2O.$$
$$MgCO_3+2HCl = MgCl_2+H_2O+CO_2; \quad FeS+2HCl = FeCl_2+H_2S.$$

In the case of metals showing variable valency, e.g. Fe, Sn, Cu, and Hg, treatment with chlorine or aqua regia yields -ic salts, and that with hydrochloric acid (when it reacts) produces -ous salt.

(c) *Insoluble chlorides,* e.g., $PbCl_2$, Hg_2Cl_2, and AgCl, are precipitated by double decomposition by the action of hydrochloric acid or sodium chloride upon a salt solution, e.g.,

$$AgNO_3+HCl = HNO_3+AgCl.$$

(d) An *-ous chloride* is converted to the *-ic state* by treatment with chlorine or aqua regia, e.g., Hg_2Cl_2+2Cl (aqua regia) $= 2HgCl_2$.

An *-ic* chloride is converted to the *-ous state* by the action of a reducing agent, e.g., nascent hydrogen, stannous chloride, sulphur dioxide, metal, etc.; e.g.,

$$HgCl_2+Hg = Hg_2Cl_2; \quad 2FeCl_3+SnCl_2 = 2FeCl_2+SnCl_4.$$
$$2CuCl_2+H_2SO_3+H_2O = Cu_2Cl_2+H_2SO_4+2HCl.$$

Properties.— (i) The chlorides are white or colourless, crystalline solids *soluble in water*, with several exception,—$CuCl_2$, $2H_2O$, and $FeCl_2$, $4H_2O$ *are green;* $FeCl_3$, $6H_2O$, *yellow*; AgCl and Hg_2Cl_2 are *amorphous powders*; stannic and plumbic chlorides are *fuming liquids;* AgCl, $PbCl_2$, Hg_2Cl_2, and Cu_2Cl_2 are *insoluble* in water—$PbCl_2$ is, however, soluble in boiling water.

(ii) When heated, hydrated chlorides generally lose water and become anhydrous, e.g., $CaCl_2,6H_2O$; but some decompose into their oxides, e.g.,;

$$MgCl_2,6H_2O = MgO + 2HCl + 5H_2O$$
$$2AlCl_3,6H_2O = Al_2O_3 + 6HCl + 9H_2O.$$

Anhydrous higher chlorides decompose into lower chlorides on heating, e.g., $2CuCl_2 = Cu_2Cl_2 + Cl_2$; $2FeCl_3 \rightleftharpoons 2FeCl_2 + Cl_2$. Chlorides of mercury sublime unchanged, and other chlorides, such as NaCl, KCl, AgCl, etc. simply *fuse* on heating.

(iii) A chloride yields chlorine on being heated with a mixture of concentrated H_2SO_4 and manganese dioxide. (p. 274).

Cu, Hg, Fe, Sn and Pb show variable valency and yield two chlorides each.

Nitrates.—Preparation.— Nitrates may be prepared: (i) by dissolving the metal in nitric acid. When a metal forms two nitrates, hot concentrated acid yields the *-ic* nitrate, and cold dilute acid the *-ous* nitrate, especially in presence of excess of the metal (p. 250).

$$Fe+4HNO_3 \text{ (hot concentrated)} = Fe(NO_3)_3+2H_2O+NO$$
$$4Fe+10HNO_3 \text{ (cold dilute)} = 4Fe(NO_3)_2+3H_2O+NH_4NO_3$$

or (ii) by dissolving the oxide, hydroxide, carbonate or sulphide in nitric acid, e.g., $CaCO_3+2HNO_3 = Ca(NO_3)_2+H_2O+CO_2$;

$$PbO+2HNO_3 = Pb(NO_3)_2+H_2O.$$

The nitrate is crystallised out from solution by concentration.

Properties.— (i) The nitrates are colourless or white (cupric nitrate is blue; ferrous nitrate $Fe(NO_3)_2$, $6H_2O$, is green), *crystalline* solids, *soluble in water.*

(ii) The nitrates decompose, on heating, into oxide of the metal, NO_2 and oxygen (except sodium and potassium nitrates which dtcompose into nitrite and oxygen) : $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$; $2NaNO_3 = NaNO_2 + O_2$.

Silver nitrate is reduced, on heating, to silver nitrite, and finally to metallic silver $2AgNO_3 = 2AgNO_2 + O_2$; $2AgNO_2 = 2Ag + 2NO + O_2$.

Sulphates.—Preparation.—Sulphates may be prepared: (i) by dissolving the metal in sulphuric acid; cold dilute acid dissolves the metals (except Pb and Al) standing above hydrogen in the electrochemical series. $Fe + H_2SO_4 = FeSO_4 + H_2$. Hot concentrated acid dissolves heavy metals, such as Pb, Cu, Ag, and Hg, yielding sulphate, sulphur dioxide and water (p. 313):

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O.$$

(ii) by dissolving the oxide, hydroxide, carbonate, or sulphide in sulphuric acid:

$$Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O\,; \quad FeS + H_2SO_4 = FeSO_4 + H_2S.$$

(iii) by roasting the sulphides in air, e.g., $ZnS + 2O_2 = ZnSO_4$.

(iv) double decomposition—*insoluble sulphates are* precipitated by the action of dilute sulphuric acid or sodium sulphate upon a salt solution: $Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3$.

Properties.—(i) The sulphates are white ($CuSO_4,5H_2O$, *blue; $FeSO_4,7H_2O$, green*), crystalline solids, *soluble in water* with several exceptions—$BaSO_4$, $SrSO_4$ and $PbSO_4$ are insoluble; $CaSO_4$, Hg_2SO_4 and Ag_2SO_4 are sparingly soluble.

(ii) Hydrated sulphates are rendered anhydrous on heating; many sulphates are decomposed by strong heat:

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3\,; \quad Ag_2SO_4 = 2Ag + SO_2 + O_2.$$

Sulphides.—Preparation.—Sulphides may be prepared: (i) by direct union by heating the metal with sulphur: $Fe + S = FeS$.

(ii) by reducing the sulphate by heating with coke:

$$Na_2SO_4 + 4C = Na_2S + 4CO\,; \quad BaSO_4 + 4C = BaS + 4CO.$$

(iii) by passing H_2S through salt solutions, when *insoluble* sulphides precipitate (p. 301): $Pb(NO_3)_2 + H_2S = PbS + 2HNO_3$.

Properties.—(i) Sulphides of alkali metals are *soluble in water;* those of the alkaline earth metals are sparingly soluble; the rest of the sulphides are insoluble. Sulphides of alkaline earth metals, Al and Cr are hydrolysed by water.

$$2CaS + 2HOH = Ca(SH)_2 \text{ (calcium hydrosulphide) } + Ca(OH)_2$$

$$Al_2S_3 + 6HOH = 2Al(OH)_3 + 3H_2S.$$

(ii) Sulphides are converted to sulphates or oxides by roasting in air:

$$ZnS + 2O_2 = ZnSO_4\,; \quad 2ZnS + 3O_2 = 2ZnO + 2SO_2.$$

(iii) Sulphides, except HgS, As_2S_3, etc., are usually decomposed by boiling HCl to yield H_2S which turns lead acetate paper black (p. 302).

$$ZnS + 2HCl = ZnCl_2 + H_2S.$$

Carbonates.—Preparation.—(i) *Insoluble carbonates* are precipitated by the action of *sodium bicarbonate* upon a salt solution—the solution is boiled for complete precipitation:

$$MgCl_2 + 2NaHCO_3 = MgCO_3 + 2NaCl + H_2O + CO_2.$$

Basic carbonates are produced owing to partial hydrolysis, if sodium carbonate is used as precipitant, except in the case of Ca and Ag. Only basic carbonates of copper and mercury (-*ic*) are known.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl.$$

Carbonates of iron (-ic), aluminium, and tin are not known; their hydroxides are only precipitated by the action of sodium carbonate upon the salt solutions, since their carbonates are completely hydrolysed by water. $2FeCl_3 + 3Na_2CO_3 + 3H_2O = 2Fe(OH)_3 + 6NaCl + 3CO_2$.

(ii) Carbonates of alkali and alkaline earth metals are produced by the action of CO_2 upon the oxides and hydroxides. Bicarbonates of these metals yield carbonate on heating.

$$2NaOH + CO_2 = Na_2CO_3 + H_2O\ ;\quad 2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Distinctive tests for carbonates and bicarbonates.—

	Carbonates	Bicarbonates
(*i*) Action of heat	Decompose giving off CO_2. [Na_2CO_3 & K_2CO_3 *melt* without decomposition]	Decompose giving off CO_2 $2NaHCO_3 \rightleftharpoons Na_2CO_3 + H_2O + CO_2$
(*ii*) Solubility in water	Insoluble; Na_2CO_3 & K_2CO_3 soluble	Soluble; $NaHCO_3$ sparingly soluble
(*iii*) *Dilute HCl	Effervescence of CO_2	Effervescence of CO_2
(*iv*) $HgCl_2$ solution	$HgCl_2 + Na_2CO_3 = HgCO_3 + 2NaCl$ Reddish-brown ppt. of basic mercuric carbonate	No precipitate
(*v*) ** $MgSO_4$ solution	White precipitate of $MgCO_3$ in the cold	No ppt. in the cold, white ppt. on boiling.

$$^{*}\ Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2\ ;\quad NaHCO_3 + HCl = NaCl + H_2O + CO_2.$$

$$^{**}\ 2NaHCO_3 + MgSO_4 = Mg(HCO_3)_2\ (\text{soluble}) + Na_2SO_4.$$

$$Mg(HCO_3)_2 \rightleftharpoons MgCO_3 + H_2O + CO_2\ (\textit{on boiling})$$

To test for bicarbonate in presence of carbonate, the latter is first precipitated by adding excess of $CaCl_2$ solution and filtered—the filtrate on being made alkaline with ammonia gives a white precipitate if a bicarbonate is present, since calcium bicarbonate, $Ca(HCO_3)_2$, is converted into $CaCO_3$ on adding ammonia.

Exercises

1. Describe, without entering into details, the various methods for the isolation of metals from their ores. Mention at least one example under each head. Give a short account of the general properties of metals. Cal. Int. 1953.

2. Write notes on: (i) flux, gangue and slag; (ii) self-reduction process; (iii) roasting and calcination.

XXVII

THE ALKALI METALS

History.—*Natron* (natural sodium carbonate) and wood ashes were used by the ancients as detergents for washing clothes. Potassium carbonate was extracted from wood ashes by water by the Arabs, and was called *al quali*, whence was derived the name *alkali* for sodium and potassium carbonates. It was discovered in the Roman period that the natural alkalis were rendered *highly corrosive and caustic* by boiling with lime, and hence the name *caustic alkali* for sodium hydroxide (caustic soda) and potassium hydroxide (caustic potash). Just to distinguish from caustic alkalis, sodium and potassium carbonates were called *mild alkalis*.

Previous to the investigations of Davy who isolated (1807) sodium and potassium by the electrolysis of fused caustic soda and potash respectively, the caustic alkalis were regarded as elements.

General characteristics.— The sub-group IA of the periodic table contains the alkali metals lithium, sodium, potassium, rubidium, and cæsium. They exhibit a gradation of physical properties, with increasing atomic weight, as the table shows :

Element	Atomic no.	Atomic wt.	At. vol.	Density	M.p. °C	B.p. °C
Lithium	3	6·94	12·9	0·52	180	1336
Sodium	11	22·997	23·7	0·97	97·5	880
Potassium	19	39·10	45·5	0·85	62·3	760
Rubidium	37	85·48	56·1	1·52	38·5	700
Cæsium	55	132·91	69·8	1·90	28·5	670

(i) The alkali metals are always found in the combined state in nature and are prepared by the same general method; *e.g.*, electrolysis of fused hydroxide or chloride.

(ii) They are light, silver-white but rapidly tarnishing in air, soft and easily fusible metals, having good conductivity for heat and electricity. Their vapour impart distinctive flame colourations; e.g., the lithium flame is red, sodium golden yellow, potassium lilac, rubidium red and cæsium blue. The vapour of alkali metals are monatomic.

(iii) They dissolve in liquid ammonia, yielding deep blue solutions.

(iv) They are the most electro-positive elements known, and hence are highly reactive—the reactivity increasing with increasing electro-positiveness from lithium to cæsium.

(v) They yield the typical oxides of the type Na_2O, which are strongly basic and dissolve in water, producing hydroxides which are strong alkalis—the basic character of oxides and hydroxides increase with increasing atomic weight.

(vi) They burn in air or oxygen to their peroxides—lithium alone yielding a monoxide, Li_2O, and sodium a mixture of monoxide, Na_2O, and peroxide. Na_2O_2.

(vii) They dissolve in cold water, yielding hydroxide and hydrogen—the reactivity of K, Rb and Cs is so great that the liberated hydrogen inflames.

(viii) They combine with hydrogen on heating yielding salt-like hydrides : *lithium alone yields a nitride when heated in nitrogen.*

(ix) The alkali metals are powerful reducing agents :

$$AlCl_3 + 3Na = Al + 3NaCl.$$

(x) The alkali metals are univalent, form colourless univalent ions, and yield salts which are freely solube in water, with few exceptions—acid sodium pyroantimonate and sodium dihydroxy tartrate are insoluble, so are potassium cobaltinitrite, potassium silicofluoride, potassium perchlorate and potassium hydrogen tartrate. Lithium carbonate, phosphate and fluoride are sparingly soluble.

(xi) Their carbonates and hydroxides are stable towards heat except Li_2CO_3 and LiOH.

(xii) Their salts with weak acids, such as carbonates and sulphides, form alkaline solutions due to hydrolysis. The sulphates, chlorides and nitrates are not hydrolysed by water.

(xiii) The alkali metal form stable acid salts, e.g.. $NaHSO_4$. They are the only metals which form *solid* bicarbonates, e.g., $NaHCO_3$—lithium bicarbonate being known in solution only.

(xiv) Their sulphides and halides have a tendency to form polysulphides (p. 299) and polyhalides, e.g., KI_3, (p. 270) respectively.

(xv) The chlorides of alkali metals form chloroplatinates, e.g., K_2PtCl_6. Their sulphates form *alums* of the type R_2SO_4, $M_2(SO_4)_3$, $24H_2O$, where R is an alkali metal and M a trivalent metal like aluminium, and *double* salts of the type $R_2SO_4,MSO_4,6H_2O$, where M is a metal like magnesium.

Sodium Na = 22·997

Occurrence.—Sodium is one of the most abundant elements, but it is never found free in nature. Its more important naturally-occurring compounds are: (i) *sodium chloride*, NaCl, in sea-water and as rock-salt, (ii) *sodium nitrate*, $NaNO_3$, in Chile saltpetre, (iii) *sodium carbonate*, Na_2CO_3. Deposits of sodium sesquicarbonate, $Na_2CO_3,NaHCO_3,2H_2O$, occur in lake Magadi in East Africa, in Egypt, as *trona*, and also in India as native *sajimati*, (iv) *soda felspar*, $Na_2O,Al_2O_3,6SiO_2$, and (v) *borax*, $Na_2B_4O_7,10H_2O$.

Though first isolated by Davy (1807) by the electrolysis of fused caustic soda, sodium was for for many years made by heating caustic soda with carbon and iron at 1000°C for want of cheap electricity.

$$2NaOH + 2C = 2Na + 2CO + H_2.$$

Metallic sodium.—Metallic sodium is now obtained by the electrolysis of either *fused caustic soda* or *sodium chloride.*

(i) Castner process.—In this process *fused* caustic soda is electrolysed using a *steel cathode* and a *nickel anode.* The caustic soda ionises into sodium and hydroxyl ions. During electrolysis sodium ions are discharged at the cathode as metallic sodium, and the OH ions at the anode as OH groups which readily decompose into water and oxygen, the latter being evolved at the anode.

$$NaOH \rightleftharpoons Na^+ + OH^-;\ Na^+ + e = Na$$

$$OH^- = OH + e;\qquad 4OH \rightleftharpoons 2H_2O + O_2.$$

Some of the water formed diffuses across to the cathode and attacks sodium, yielding hydrogen—the efficiency of the process is being lowered thereby, since some sodium is lost. But the principal disadvantage of the process is the relatively high cost of caustic soda. The cell is narrow at the bottom

An iron vessel (fig. 157) contains the caustic soda which is fused initially by gas burners (m. pt. of sodium hydroxide 318°), but the process of electrolysis once started, the required temperature of the bath, 327°, is maintained by the heating effect of the current. (The steel cathode is led into the bath from below and held in position in the neck of the pot by solid caustic soda); the cathode is screened by an iron wire gauze, suspended from an iron cylinder. The anode is a nickel cylinder that surrounds the cathode and forms a part of the cover, being insulated by asbestos rings from the iron bath, and from the iron cylinder in which sodium collects. During electrolysis sodium is liberated at the cathode and collects in the iron cylinder

Cathode is a steel bar inserted through the bottom of the bath and held firmly by solid NaOH

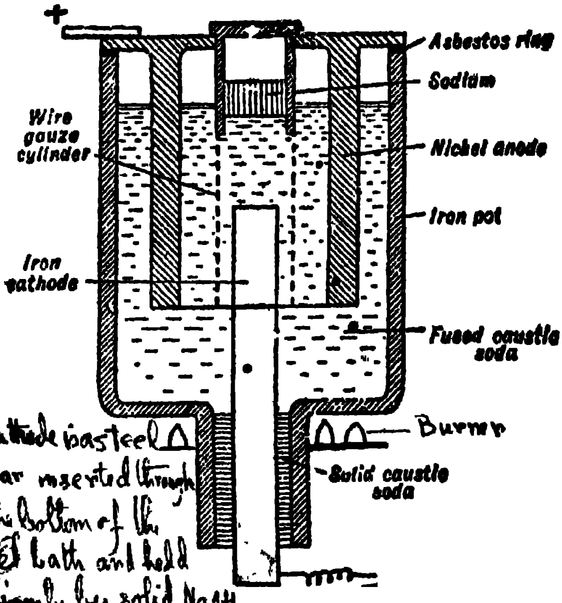


Fig. 157

sodium hydroxide (caustic soda) and potassium hydroxide (caustic potash). Just to distinguish from caustic alkalis, sodium and potassium carbonates were called *mild alkalis.*

Previous to the investigations of Davy who isolated (1807) sodium and potassium by the electrolysis of fused caustic soda and potash respectively, the caustic alkalis were regarded as elements.

General characteristics.— The sub-group IA of the periodic table contains the alkali metals lithium, sodium, potassium, rubidium, and cæsium. They exhibit a gradation of physical properties, with increasing atomic weight, as the table shows :

Element	Atomic no.	Atomic wt.	At. vol.	Density	M.p. °C	B.p. °C
Lithium	3	6·94	12·9	0·52	180	1336
Sodium	11	22·997	23·7	0·97	97·5	880
Potassium	19	39·10	45·5	0·85	62·3	760
Rubidium	37	85·48	56·1	1·52	38·5	700
Cæsium	55	132·91	69·8	1·90	28·5	670

(i) The alkali metals are always found in the combined state in nature and are prepared by the same general method; *e.g.*, electrolysis of fused hydroxide or chloride.

(ii) They are light, silver-white but rapidly tarnishing in air, soft and easily fusible metals, having good conductivity for heat and electricity. Their vapour impart distinctive flame colourations; e.g., the lithium flame is red, sodium golden yellow, potassium lilac, rubidium red and cæsium blue. The vapour of alkali metals are monatomic.

(iii) They dissolve in liquid ammonia, yielding deep blue solutions.

(iv) They are the most electro-positive elements known, and hence are highly reactive—the reactivity increasing with increasing electro-positiveness from lithium to cæsium.

(v) They yield the typical oxides of the type Na_2O, which are strongly basic and dissolve in water, producing hydroxides which are strong alkalis—the basic character of oxides and hydroxides increase with increasing atomic weight.

(vi) They burn in air or oxygen to their peroxides—lithium alone yielding a monoxide, Li_2O, and sodium a mixture of monoxide, Na_2O, and peroxide, Na_2O_2.

(vii) They dissolve in cold water, yielding hydroxide and hydrogen—the reactivity of K, Rb and Cs is so great that the liberated hydrogen inflames.

(viii) They combine with hydrogen on heating yielding salt-like hydrides : *lithium alone yields a nitride when heated in nitrogen.*

(ix) The alkali metals are powerful reducing agents :

$$AlCl_3 + 3Na = Al + 3NaCl.$$

(x) The alkali metals are univalent, form colourless univalent ions, and yield salts which are freely solube in water, with few exceptions—acid sodium pyroantimonate and sodium dihydroxy tartrate are insoluble, so are potassium cobaltinitrite, potassium silicofluoride, potassium perchlorate and potassium hydrogen tartrate. Lithium carbonate, phosphate and fluoride are sparingly soluble.

(xi) Their carbonates and hydroxides are stable towards heat except Li_2CO_3 and LiOH.

(xii) Their salts with weak acids, such as carbonates and sulphides, form alkaline solutions due to hydrolysis. The sulphates, chlorides and nitrates are not hydrolysed by water.

(xiii) The alkali metal form stable acid salts, e.g., $NaHSO_4$. They are the only metals which form *solid* bicarbonates, e.g., $NaHCO_3$—lithium bicarbonate being known in solution only.

(xiv) Their sulphides and halides have a tendency to form polysulphides (p. 299) and polyhalides, e.g., KI_3, (p. 270) respectively.

(xv) The chlorides of alkali metals form chloroplatinates, e.g., K_2PtCl_6. Their sulphates form *alums* of the type R_2SO_4, $M_2(SO_4)_3$, $24H_2O$, where R is an alkali metal and M a trivalent metal like aluminium, and *double* salts of the type $R_2SO_4,MSO_4,6H_2O$, where M is a metal like magnesium.

Sodium $Na = 22{\cdot}997$

Occurrence.—Sodium is one of the most abundant elements, but it is never found free in nature. Its more important naturally-occurring compounds are: (i) *sodium chloride*, NaCl, in sea-water and as rock-salt, (ii) *sodium nitrate*, $NaNO_3$, in Chile saltpetre, (iii) *sodium carbonate*, Na_2CO_3. Deposits of sodium sesquicarbonate, $Na_2CO_3,NaHCO_3,2H_2O$, occur in lake Magadi in East Africa, in Egypt, as *trona*, and also in India as native *sajimati*, (iv) *soda felspar*, $Na_2O, Al_2O_3,6SiO_2$, and (v) *borax*, $Na_2B_4O_7,10H_2O$.

Though first isolated by Davy (1807) by the electrolysis of fused caustic soda, sodium was for for many years made by heating caustic soda with carbon and iron at 1000°C for want of cheap electricity.

$$2NaOH + 2C = 2Na + 2CO + H_2.$$

Metallic sodium.—Metallic sodium is now obtained by the electrolysis of either *fused caustic soda* or *sodium chloride.*

(i) Castner process.—In this process *fused* caustic soda is electrolysed using a *steel cathode* and a *nickel anode.* The caustic soda ionises into sodium and hydroxyl ions. During electrolysis sodium ions are discharged at the cathode as metallic sodium, and the OH ions at the anode as OH groups which readily decompose into water and oxygen, the latter being evolved at the anode.

$$NaOH \rightleftharpoons Na^+ + OH^- ;\ Na^+ + e = Na$$

$$OH^- = OH + e ;\qquad 4OH \rightleftharpoons 2H_2O + O_2.$$

Some of the water formed diffuses across to the cathode and attacks sodium, yielding hydrogen—the efficiency of the process is being lowered thereby, since some sodium is lost. But the principal disadvantage of the process is the relatively high cost of caustic soda. The cell in narrow at the bottom

An iron vessel (fig. 157) contains the caustic soda which is fused initially by gas burners (m. pt. of sodium hydroxide 318°), but the process of electrolysis once started, the required temperature of the bath, 327°, is maintained by the heating effect of the current. (The steel cathode is led into the bath from below and held in position in the neck of the pot by solid caustic soda); the cathode is screened by an iron wire gauze, suspended from an iron cylinder. The anode is a nickel cylinder that surrounds the cathode and forms a part of the cover, being insulated by asbestos rings from the iron bath, and from the iron cylinder in which sodium collects. During electrolysis sodium is liberated at the cathode and collects in the iron cylinder

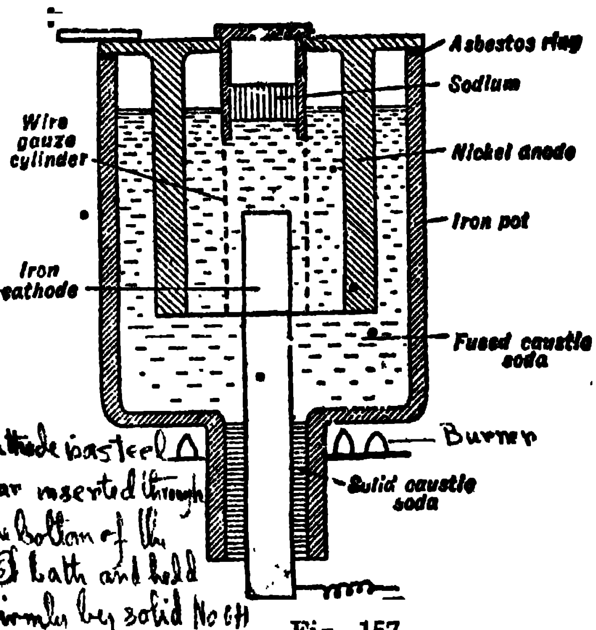


Fig. 157

Cathode is a steel bar inserted through the bottom of the bath and held firmly by solid NaOH in the molten state, floating on the surface of molten caustic soda—the hydrogen, also collecting in the same vessel, prevents the sodium from oxidation. Sodium is removed from time to time by means of a spoon of nickel wire gauze which retains the sodium but allows the caustic soda to run back. The oxygen liberated at the anode is a valuable by-product.)

$NaCl + \frac{1}{4}$th . $CaCl_2$

The discharge potential of Ca is higher than Na, therefore electro-liberation of Na occurs first

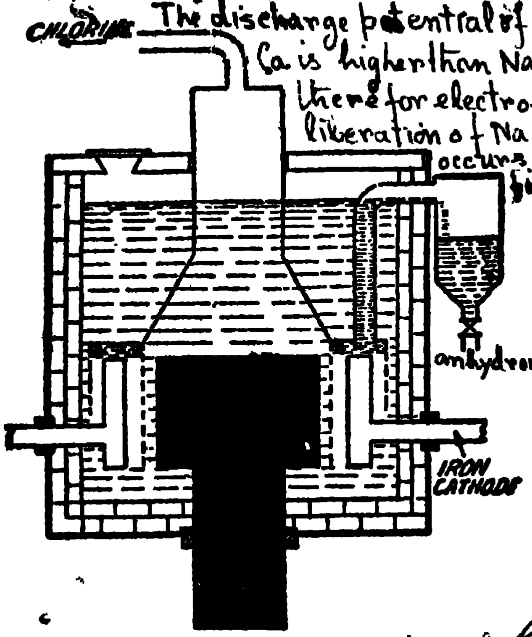


Fig. 158

anhydrous

porcelain

(ii) **Downs process.**— Sodium chloride is the cheapest source of sodium. But the electrolysis of fused sodium chloride is ordinarily met with many difficulties arising from its high melting point, 803°. Above 800° the sodium chloride and the liberated chlorine are highly corrosive, and the sodium is volatile (b. pt. 880°), and the metal forms a 'metallic fog' with the molten salt, which it is difficult to condense. In the Downs process, worked out in 1924 by Downs in America, fused sodium chloride, containing sufficient calcium chloride to reduce the melting point of the salt from 800° to 650°, at which temperature no 'metallic fog' formation takes place, is electrolysed in an iron vessel (fig. 158) lined inside with firebricks. Chlorine is evolved at the graphite anode set in the centre of the cell, and is led out by a conical collecting hood which is placed above the anode. The cathode is an iron cylinder surrounding the anode—a mantle of two iron-gauze screens separates the anode from the cathode. The sodium set free at the cathode rises to the suface of the electrolyte and is led out by an iron pipe, fitted at the top of the mantle, into a closed receiver. $NaCl \rightleftharpoons Na^+ + Cl^-$. For comparison of Castner and Down

At cathode $Na^+ + e = Na$; At anode $Cl^- = Cl + e$. See Chitta Mitra

Properties.—(i) Sodium is a light (lighter than water), soft (and hence may be squeezed through an orifice in the form of sodium wire), silver-white metal with a good conductivity for heat and electricity.

(ii) Stable in dry air, it readily *tarnishes in moist air* due to the formation of a film of oxide, which gradually turns into a mixture of hydroxide and carbonate, and hence *the metal is kept under kerosene oil.*

(iii) It burns in air with a bright *yellow flame*, yielding a mixture of monoxide and peroxide: $4Na+O_2 = 2Na_2O$; $2Na+O_2 = Na_2O_2$.

(iv) It burns in chlorine on heating, yielding sodium chloride—perfectly *dry* chlorine does not attack the metal.

(v) It decomposes cold water, yielding hydrogen and caustic soda:

$$2Na+2HOH = 2NaOH+H_2.$$

(vi) It reacts with dry ammonia at 300° to 400°, yielding *sodamide*, $NaNH_2$, which is decomposed by water, liberating ammonia:

$$2Na+2NH_3 = 2NaNH_2+H_2;\ NaNH_2+H_2O = NaOH+NH_3.$$

(vii) It reacts with hydrogen at 360°, yielding *sodium hydride*, which is decomposed by water, setting free hydrogen:

$$2Na + H_2 = 2NaH; \quad NaH + HOH = H_2 + NaOH.$$

(viii) Ignited sodium decomposes carbon dioxide, depositing carbon:

$$3CO_2 + 4Na = 2Na_2CO_3 + C.$$

(ix) It is a powerful reducing agent: $3Na + AlCl_3 = Al + 3NaCl$.

(ix) It dissolves in mercury, yielding a liquid amalgam. It dissolves in liquid ammonia giving a deep blue solution. Sodium amalgam is prepared by pressing small pieces of sodium into mercury in a mortar with a pestle.

Uses of sodium.— (i) In the manufacture of sodium peroxide, sodamide, and sodium cyanide; (ii) As a reducing agent in synthetic organic chemistry, for example in the manufacture of artificial *indigo*. Sodium amalgam is also used as a reducing agent.

Compounds of Sodium

Sodium monoxide, Na_2O, is obtained by burning sodium at 180° in a limited supply of air or oxygen and distilling off the excess of sodium in vacuo, or by heating sodium peroxide, nitrate or nitrite with sodium:

$$Na_2O_2 + 2Na = 2Na_2O; \quad 2NaNO_3 + 10Na = 6Na_2O + N_2.$$

A white amorphous mass, it decomposes at 400° into sodium peroxide and sodium, and dissolves violently in water, yielding caustic soda:

$$Na_2O + H_2O = 2NaOH.$$

Sodium peroxide, Na_2O_2, is formed by heating the metal in excess of air or oxygen. It is made by heating thin slices of sodium in aluminium trays in a current of purified air, (freed from moisture and CO_2) at 300° in an iron tunnel—the temperature is controlled by moving the trays in opposite direction to the air current. External heating is required only to start the reaction:

$$2Na + O_2 = Na_2O_2 + 119{,}800 \text{ calories.}$$

Properties.—(i) Sodium peroxide is a *yellow solid*, becoming white in air from the formation of a film of sodium hydroxide and carbonate.

(ii) It dissolves in *ice-cold water* with hydrolysis, yielding hydrogen peroxide, which decomposes into water and oxygen on warming; it gives oxygen and caustic soda with water at room temperature:

$$Na_2O_2 + 2H_2O \rightleftharpoons 2NaOH + H_2O_2; \quad 2Na_2O_2 + 2H_2O = 4NaOH + O_2.$$

A crystalline hydrate, $Na_2O_2,8H_2O$, may be separated from ice-water.

(iii) It dissolves in *ice-cold* dilute mineral acids, yielding hydrogen peroxide: $Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2$.

(iv) It reacts with carbon dioxide, giving sodium carbonate and oxygen, and hence its use for purifying air in a closed space:

$$2Na_2O_2 + 2CO_2 = 2Na_2CO_3 + O_2.$$

(v) It is a powerful oxidising agent; thus it violently attacks charcoal at 300°—400°, depositing metallic sodium:

$$3Na_2O_2 + 2C = 2Na_2CO_3 + 2Na.$$

A mixture of sodium peroxide and moist sawdust readily inflames. In the fused state it attacks most metals, including silver and platinum—nickel is less readily attacked, and hence *the use of nickel crucibles in sodium peroxide fusion.*

Uses.— (i) In the manufacture of hydrogen peroxide; (ii) for bleaching (after acidification) delicate fabrics, such as silk, wool, etc.; (iii) for preparing oxygen; (iv) for oxygenating the air in submarines; (v) as an oxidising agent in the laboratory. A little copper oxide is mixed with sodium peroxide and sold under the name 'oxone' for preparing oxygen.

Sodium hydroxide, caustic soda, *NaOH*, is manufactured either by the electrolysis of sodium chloride or by causticising sodium carbonate with lime.

Electrolysis of sodium chloride solution yields caustic soda, hydrogen and chlorine (p. 123). Sodium hydroxide and hydrogen formed at the cathode must be kept separated from chlorine produced at the anode, in order to prevent the formation of hypochlorite and of explosive mixture of hydrogen and chlorine. The separation is effected either *by using a mercury cathode or a porous diaphragm.*

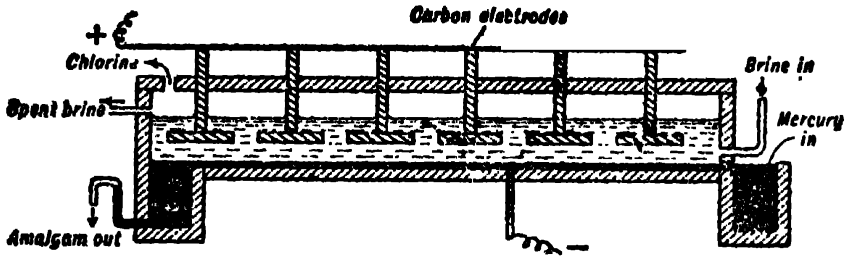


Fig. 159

The mercury cathode cell.— In the *Kellner-Solvay* cell (fig. 159) (modified *Castner-Kellner cell*) a stream of brine (aqueous solution of sodium chloride) is electrolysed between graphite anodes and a mercury cathode, which flows slowly in thin layer across the floor of the cell (a rectangular cement trough)—brine flows in the same direction as the mercury. Chloride ions Cl^- are discharged at the anode to form chlorine which is drawn away through earthenware pipes to be liquefied or used in making HCl, bleaching powder and sodium hypochlorite etc. Na^+ ions are discharged at the cathode in preference to H^+ ions, yielding sodium, which dissolves in mercury to form a dilute liquid sodium amalgam.

The sodium amalgam flows into a lower tank, where it is decomposed by water, yielding caustic soda and hydrogen, in contact with metallic iron—the amalgam and iron forming a short-circuited cell:

$$^{-}\text{Na-amalgam} \mid \text{NaOH solution} \mid \text{Fe}^{+}$$

Sodium from the amalgam passes into solution as sodium ions: $Na = Na^+ + e$, and the electrons pass through the mercury to the iron; the hydrogen ions from water ($H_2O \rightleftharpoons H^+ + OH^-$) are discharged by the electrons on the iron surface, which evolve as gas:

$$H^+ + e = H; \quad 2H = H_2.$$

The overall reactions are:

In the primary cell, $2NaCl + 2xHg = 2NaHgx + Cl_2$.

In the secondary cell, $2NaHgx + 2H_2O = 2NaOH + H_2 + 2xHg$.

The solution, therefore, contains Na^+ and OH^- ions, i.e., sodium hydroxide. When the solution contains 40% caustic soda, it is evaporated, fused, and run into iron drums to solidify or cast into sticks. The mercury freed from sodium is sent back into the electrolytic cell.

The spent brine is saturated with more salt, and then returned to the cell.

The process yields a pure concentrated solution of caustic soda. But it is more expensive than other electrolytic processes, because of high cost of mercury, and of the comparatively high voltage required by the cell.

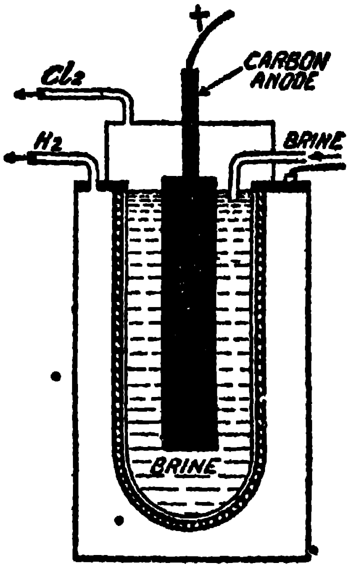


Fig 160

The diaphragm cells.— Typical of this class is the Nelson cell which is extensively employed. It consists of a U-shaped vessel (fig. 160) made of asbestos and contains the graphite anode. The cathode is made of perforated sheet steel covering the outer surface of the asbestos walls, which constitute the diaphragm. The cell is placed in an outer case, which is kept full of steam—the steam heats the liquor, reduces its resistance, and also keeps the pores of the diaphragm clear. The cell is fed with *purified* brine, which is kept at a constant level by an automatic device—the brine must be freed from salts of iron and other metals which would give insoluble hydroxides with caustic sida, and so clog the diaphragm. The brine percolates by gravity through the asbestos, where it undergoes electrolysis. The Cl' ions are discharged at the anode and the chlorine gas is led off. H^+ ions are discharged at the cathode, while Na^+ and OH^- ions, *i.e.,* sodium hydroxide, accumulate in the water which diffuses through the porous diaphragm from the anode compartment. The alkali concentration is only 10–12%, the liquor containing 14–16% NaCl, which is separated as solid by concentration in vacuum evaporators, and the concentrated caustic liquor finally evaporated and fused.

The installation cost and the voltage requirement of the diaphragm cell are less than the mercury-cathode process. But it yields a less concentrated alkali, containing a good deal of common salt.

Causticising of sodium carbonate.—Gossage's mehhod: When calcium hydroxide is added to sodium carbonate solution, calcium carbonate is precipitated, leaving sodium hydroxide in solution :

$$Na_2CO_3 + Ca(OH_2) \rightleftharpoons 2NaOH + CaCO_3.$$

The reaction is incomplete in concentrated solutions, since calcium hydroxide is but sparingly soluble in a strong solution of caustic soda : *a dilute solution* of sodium carbonate is, therefore, causticised. On a large scale, a 10% solution of soda ash is taken in an iron tank—lumps of lime are suspended in the solution in an iron cage. The solution is stirred by mechanical agitators, and heated by *open* steam. The reaction complete in about an hour's time, the sludge of chalk and excess lime is allowed to settle, and the clear caustic liquor is run off. The liquor is concentrated in vacuum evaporators, where the unchanged sodium carbonate separates and is removed. The concentrated sodium hydroxide solution is evaporated to dryness, fused and run into drums to solidify.

A large amount of caustic soda is still obtained by this process, since its production by electrolytic method is limited by the demand for chlorine.

Purification of sodium hydroxide.— Sodium hydroxide obtained by the above methods is liable to contain sodium chloride, carbonate, and sulphate in small amounts. This is purified by treatment with alcohol which dissolves the hydroxide, but not the salts, and then evaporating the solution in a silver dish. Pure caustic soda free from sodium carbonate is best obtained by dissolving sodium in water.

Properties.—(i) Sodium hydroxide is a white, crystalline, deliquescent, highly corrosive solid (m. p. 318°), which readily absorbs CO_2 from the air, forming sodium carbonate. *A powerful cautery*, it attacks the proteins of the skin.

(ii) *Stable towards heat,* it is reduced in the fused state to metal, when heated with carbon: $2NaOH+2C = 2Na+2CO+H_2$.

The presence of hydrogen in caustic soda (or potash) may be shown by fusing the latter with iron filings in a test tube—the evolved hydrogen being ignited at a jet fixed to the tube. The iron is oxidised and sodium also distils off: $2NaOH + 2Fe = 2FeO + 2Na + H_2$.

(iii) *A strong base,* it readily dissolves in water (42 gms. in 100 gms. of water at 0°) giving a strongly alkaline solution with a soapy touch. The aqueous solution precipitates the hydroxides or oxides of heavy metals, from solutions of their salts, and liberate ammonia from ammonium salts: $FeCl_3+3NaOH = Fe(OH)_3+3NaCl$;

$$NH_4Cl+NaOH = NaCl+NH_3+H_2O.$$

The hydroxides of Zn, Al, Sn, and Pb are soluble in excess of caustic soda: $Zn(OH)_2+2NaOH = Na_2ZnO_2$ (sodium zincate) $+2H_2O$.

(iv) It dissolves acidic and amphoteric oxides, yielding salts: $CO_2+2NaOH = Na_2CO_3+H_2O$; $Al_2O_3+2NaOH = 2NaAlO_2+H_2O$.

Materials containing *silica*, such as *glass*, are rapidly attacked by fused caustic soda, and slowly by aqueous alkali, silica being dissolved as sodium silicate:

$$SiO_2 + 2NaOH = Na_2SiO_3 + H_2O.$$

(v) Aqueous sodium hydroxide dissolves B, Si, Zn, Al and Sn, yielding salt and hydrogen; several non-metals, such as P, S, Cl, etc., yield a hydride (or a salt of the hydride) instead of hydrogen.

$4P+3NaOH+3H_2O = PH_3+3NaH_2PO_2$ (sodium hypophosphite).

$2Al+2NaOH+2H_2O = 2H_2+2NaAlO_2$ (sodium aluminate).

Nearly all metals are attacked by fused caustic alkali; Fe, Ni, Ag, Au and Pt are the most resistant to attack.

Uses of sodium hydroxide.—It is used: (i) in the manufacture of sodium, soap and sodium formate; (ii) in the purification of bauxite; (iii) in the manufacture of paper, artificial silk and dyes; (iv) in the refining of petroleum; (v) in making alkaline bleach; (vi) as a cleansing agent for machines, metal sheets, etc., since it emulsifies oil and grease; *is is too caustic for use in washing.*

Sodium carbonate, Na_2CO_3.— It occurs in and around certain lakes, notably at Magadi in British East Africa, and in Lower Egypt. The Magadi deposit, containing some 200 million tons of native soda, forms an important source of soda supply.

Sodium carbonate was formerly obtained from the ash of plants growing on sea-shore. But the method was superseded early in the nineteenth century by the *Leblanc process,* discovered by Nicholas Leblanc in 1787, as a result of an offer of prize by the French Academy of science for the preparation of alkali from common salt.

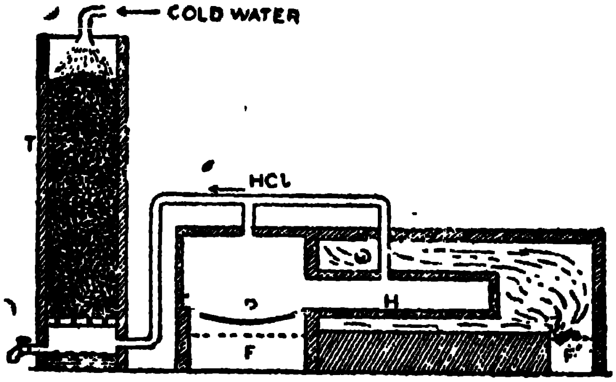


Fig. 161

The Leblanc process.—The main features of the process are :

(i) **Production of salt cake.**—Sodium chloride is converted to sodium sulphate by the action of concentrated sulphuric acid, in two stages in a gas-tight furnace (fig. 161) containing an iron pan P and a hearth H (a fire-clay box, called *muffle*). The charge of equal quantities of salt and acid is first heated in the pan, yielding sodium bisulphate and hydrochloric acid. The pasty mass from the pan is then raked out and strongly heated in the hearth, yielding sodium sulphate, called *salt-cake.*

$$NaCl + H_2SO_4 = NaHSO_4 + HCl \text{ (in the pan).}$$

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl \text{ (in the hearth).}$$

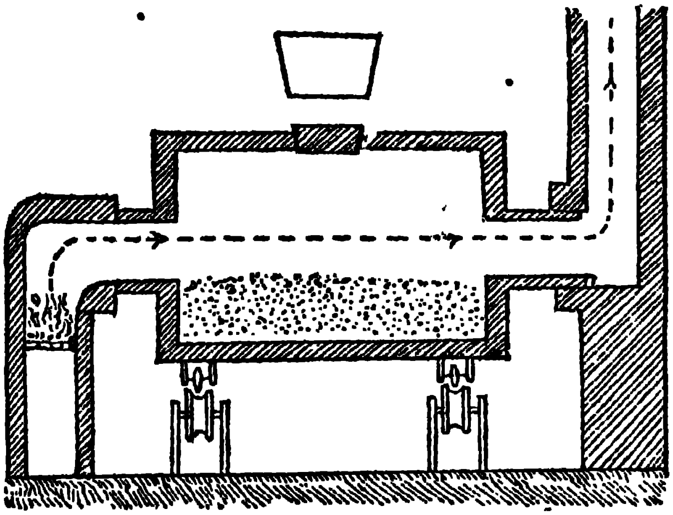


Fig. 162

The HCl gas is absorbed by water trickling over coke in a tower, giving commercial hydrochloric acid.

(ii) **Conversion of salt-cake into black ash.**—The salt cake is ground, and mixed with its own weight of limestone and half its weight of coal, and strongly heated to 800°—1000° in a rotating furnace (fig. 162). The salt cake is reduced by coke to sulphide, which reacts with calcium carbonate, yielding sodium carbonate and calcium sulphide :

$$Na_2SO_4 + 4C = Na_2S + 4CO\,; \quad Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The product is called *black ash* and contains 45% sodium carbonate.

(iii) **Lixiviation of black ash.**——The black ash is lixiviated with water in a series of tanks on a counter-current principle. The extract contains sodium carbonate and also some caustic soda. Hence it is either, (a) converted to caustic soda by causticising with lime, or (b) freed from caustic soda by treatment with CO_2, and then crystallised out as **soda crystals** or **washing soda,** $Na_2CO_3, 10H_2O$; the soda crystals on calcination gives anhydrous sodium carbonate, **soda ash.**

The **alkali waste,** left after extracting soda. contains calcium sulphide, and may be used for sulphur recovery.

The Leblanc process as a whole is obsolete; only the first step is worked to provide salt-cake for glass making.

The Ammonia-soda process, or Solvay process. About the middle of the nineteenth century the Solvay process gradually became a serious rival of the Leblanc process, which it ultimately displaced. Nearly all the sodium carbonate is now manufactured by the Solvay process.

The principle of the progess is that, when an excess of carbon dioxide is bubbled through nearly saturated solution of common salt (brine) containing ammonia, ammonium bicarbonate is formed; this then reacts with the sodium chloride yielding *sparingly soluble sodium bicarbonate* and ammonium chloride. The sodium bicarbonate is separated by filtration and calcined to give sodium carbonate and carbon dioxide. $NH_3 + CO_2 + H_2O \rightleftharpoons NH_4HCO_3$;

$$NH_4HCO_3 + NaCl \rightleftharpoons NaHCO_3 + NH_4Cl.$$

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

About two-thirds of the common salt is converted into sodium bicarbonate, as the reaction is reversible.

The ammonium chloride in the filtrate is boiled with lime in a still to regenerate ammonia, which is used again, to saturate fresh brine.

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + 2H_2O + CaCl_2.$$

The lime is obtained by heating limestone with coke in a kiln. $CaCO_3 = CaO + CO_2$. The CO_2 produced, together with that obtained by calcining sodium bicarbonate, is used for carbonating ammoniacal brine.

The process depends upon the supply of the raw materials brine, limestone and coal. The process is carried out as follows :

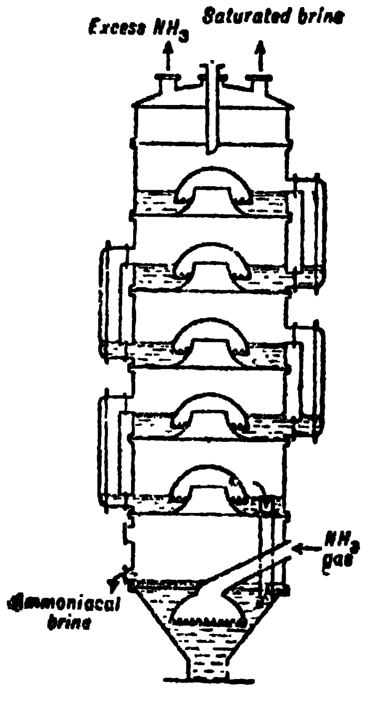


Fig. 163

(i) **Preparation of ammoniacal brine.**—The brine trickles down a tower (fig. 163) fitted with a number of partitions, in which ammonia enters at the bottom.

The brine forms a layer on the floor of each compartment and flows down vertical pipes from one compartment to the next below; ammonia is made to pass up the centre of the tower, and stream through the brine on each floor by means of a series of hoods. The brine gets saturated with ammonia, and at the same time *salts of Ca, Mg* and *Fe* present in the brine are precipitated as carbonates by carbon dioxide (always contained in the ammonia from the still). The ammoniacal brine, passing out at the bottom, is allowed to settle out in a settling tank, whence it is led to a *cooler*, and then to the carbonating tower.

(ii) **Carbonation.**—The carbonation is carried out in Solvay's tower (fig. 164) which is fitted with a number of partitions, each having a central hole covered by a perforated hood. The ammoniacal brine is introduced at the top so as to *completely fill* the lower part of the tower, and carbon dioxide is forced under pressure at the base. The carbon dioxide is uniformly distributed through the solution in small bubbles, and a perfect absorption takes place. Heat is evolved in the reaction, and since the solubility of bicarbonate increases with rise in temperature, the tower is cooled by circulation of cold water through coils fitted in the lower part—the temperature is kept at 30°-40°, but is reduced to about 15° towards the end. The sodium bicarbonate precipitates and passes out with solution at the base.

(iii) **Filtration.**—The sodium bicarbonate is separated by filtration by a *rotary suction filter* which is essentially a sheet of flannel stretched on a wire-gauze drum; the drum is half submerged in the solution and kept in slow rotation—vacuum being maintained on the inside. The bicarbonate deposits on the flannel: It is scrapped out after washing with a spray of water, and then dried.

(iv) **Calcination.**—The bicarbonate is calcined in a closed pan fitted with an exit to remove carbon dioxide. The last traces of CO_2 are removed by raking the calcined mass through a long trough heated by fire below. The *soda ash,* thus produced, is of 99·5 per cent purity.

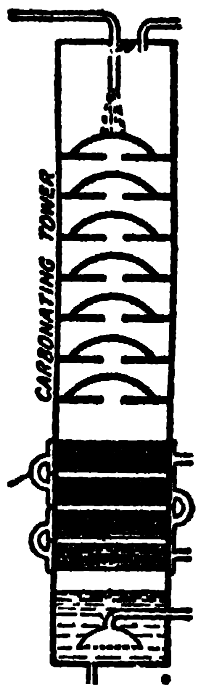


Fig. 164

Electrolytic process.—Sodium carbonate is made by the electrolysis of sodium chloride solution in **Hargreaves—Bird diaphragm cell** (fig. 165). The cell is an iron box made into three compartments by asbestos partitions which act as porous diaphragms. The central compartment it fitted with gas carbon anode, while the cathodes are copper gauze which press against the outside of the diaphragm. Purified brine is contimuously fed into the anode chamber near the bottom—the spent brine leaving at the top. During electrolysis Cl^- ions are discharged at the anode and the chlorine gas is led away. H^+ ions are discharged at the cathode and hydrogen is led away—Na^+ and OH^- ions, i.e., caustic soda, accumulate in the water in the cathode chambers by diffusion through the diaphragm from the anode compartment. Steam and carbon dioxide are injected into the cathode compartments, where caustic soda reacts with carbon dioxide, yielding a solution of sodium carbonate—the liquor containing 170g. of Na_2CO_3 and 3·6g. NaCl per litre. The solution yields soda crystals on evaporation.

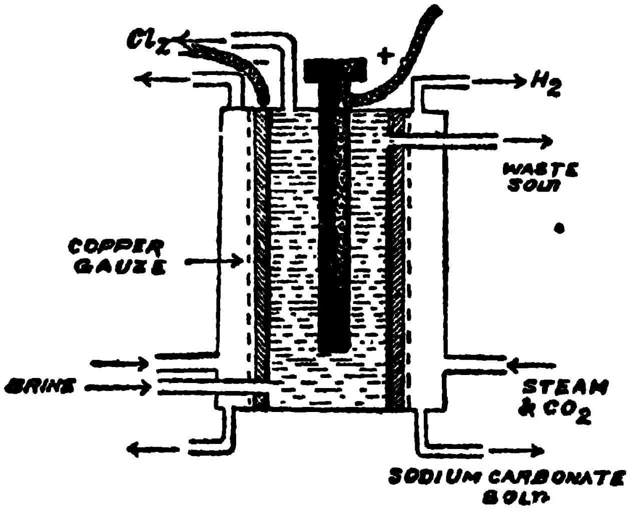


Fig. 165

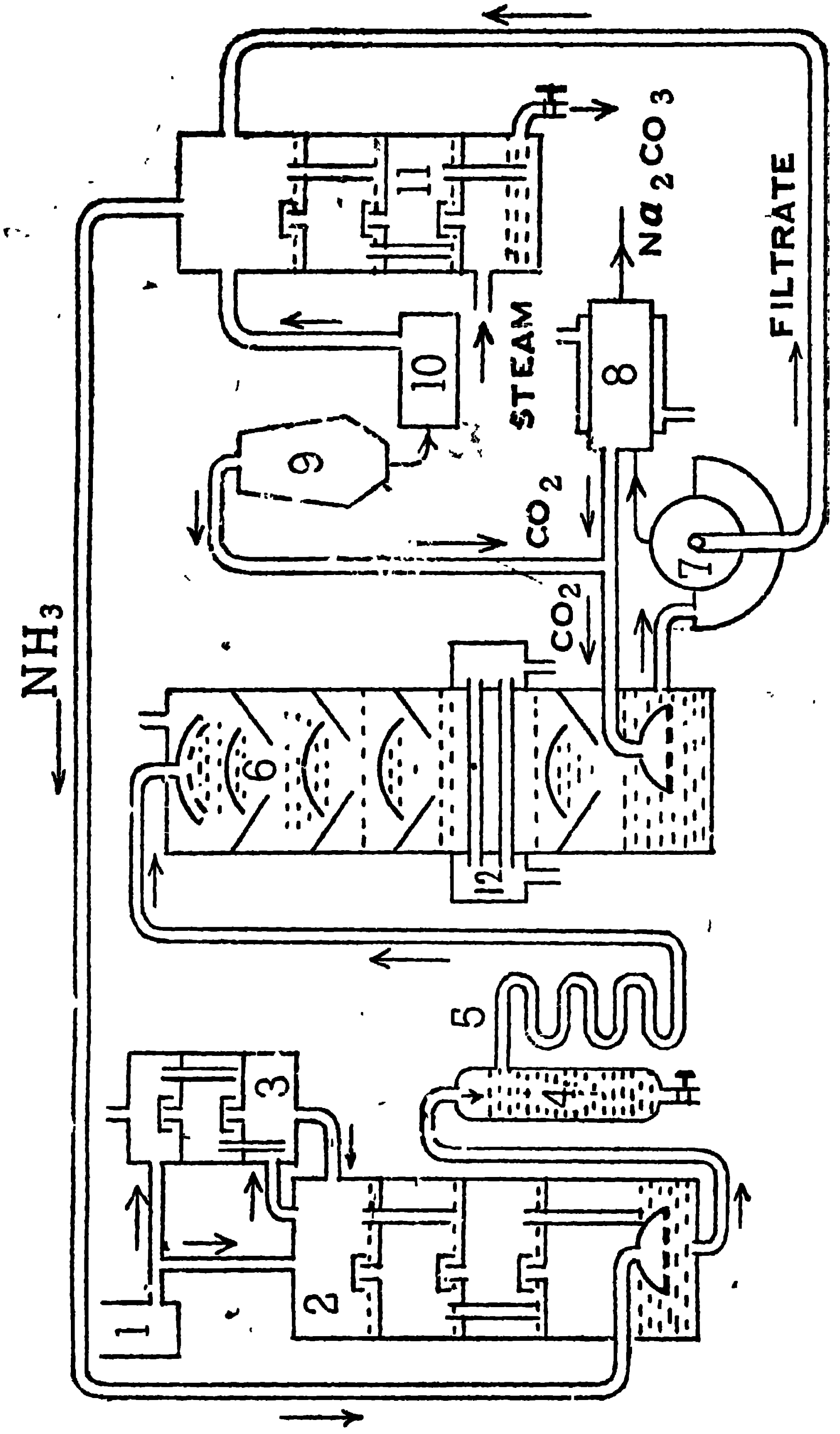


Fig. 166

The Solvay process unit (fig. 166).

1 brine tank; 2 & 3 ammonia scrubber; 4 settling tank; 5 cooler; 6 Solvay tower; 7 filter; 8 roaster; 9 lime klin; 10 lime slaker; 11 ammonia still.

Advantage of the Solvay process.— The Solvay process has completely displaced the old Leblanc process, since

(i) it delivers soda of much higher purity;

(*ii*) the process is less expensive, since brine is directly used, and no sulphuric acid is required;

(*iii*) the operation is continuous, and cleaner, since no noxious HCl is evolved, as in the Leblanc process;

(*iv*) the consumption of fuel is less, since there are no solutions to be evaporated as in Leblanc process;

(*v*) the efficiency of the process is higher—the ammonia and carbon dioxide are recovered and used again.

The disadvantages of the process are (i) the whole of chlorine of the common salt is lost as calcium chloride, for which there is no adequate market yet; (ii) the high cost of ammonia for replacing the losses.

Recently the Solvay process has been greatly improved by Hou and coupled with synthetic ammonia process. In this case there is no need for ammonia recovery. The bicarbonate mother liquor is agitated with dry common salt when ammonium chloride precipitates and is filtered—the filtrate which now contains NaCl, is made into ammoniacal brine and carbonated as usual.

In this process the conversion of salt into soda is 96% or higher, and the chlorine of the sodium chloride is completely utilised as ammonium chloride which forms an excellent fertiliser. The process offers a method of fixing ammonia as ammonium chloride.

The production of soda by the electrolytic process is limited by the demand for chlorine, which is at present very much less than that for the alkali. The by-product chlorine is mainly used for obtaining bleach, and hydrochloric acid. With new avenues for the utilisation of chlorine, the electrolytic process has a promise in future. The Solvay process is yet the most important one for soda manufacture.

Soda ash and caustic soda are the two key chemicals indispensable for the industrial planning of a country. The Mettur Chemical Works, Madras, and the Tata Chemicals Ltd. at Mithapur near Okha are of late producing the much needed alkalis. The Imperial Chemical Industries Ltd. manufacture caustic soda at Rishra near Calcutta, using diaphragm cell. Besides, many paper mills produce caustic soda and chlorine for their internal consumption; e.g., Rhotas Industries at Dehri-on-Sone use Kellner-Solvay cell; Titaghur Paper Mills in Bengal employ *Nelson cell.*

Properties of sodium carbonate.— (i) Anhydrous sodium carbonate, called **soda ash,** is a white powder, which *melts* without decomposition at 852°, and absorbs moisture from air, forming the monohydrate, Na_2CO_3, H_2O.

(ii) It dissolves in water giving an alkaline solution owing to hydrolysis: $Na_2CO_3 + H_2O \rightleftharpoons NaOH + NaHCO_3$.

The aqueous solution on evaporation yields crystals of **washing soda,** $Na_2CO_3, 10H_2O$, which effloresce in air, giving **crystal-carbonate,** Na_2CO_3, H_2O.

(iii) The aqueous solution absorbs CO_2, yielding *sparingly soluble sodium bicarbonate,* which is filtered, washed, dried and calcined at 250°—300° to give *pure sodium carbonate.*

$$Na_2CO_3 + H_2O + CO_2 \rightleftharpoons 2NaHCO_3.$$

Concentrated soda crystal, used in wool washing, is the sesquicarbonate, $Na_2CO_3, NaHCO_3, 2H_2O$ (native *trona*). Sodium bicarbonate is used in medicine to reduce stomachic acidity and in baking powder.

(iv) It dissolves in dilute mineral acids with an effervescense of carbon dioxide: $Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$.

(v) It is causticised by lime to give caustic soda.

On being heated with ferric oxide, it yields sodium ferrite, which on treatment with hot water gives caustic soda. This is the principle of now-obsolete *Lowing process*:

$$Na_2CO_3 + Fe_2O_3 = 2NaFeO_2 + CO_2;\ 2NaFeO_2 + H_2O = 2NaOH + Fe_2O_3.$$

Uses of sodium carbonate.— It is used : (i) in the manufacture of glass, soap and caustic soda; (*ii*) for washing textile fabrics; (*iii*) in the softening of water; (*iv*) for the preparation of other sodium salts; and (*v*) as a reagent in the laboratory.

Sodium chloride or *common salt*, NaCl, occurs abundantly in nature as *rock salt* or else in solution as *brine*, containing about 25% sodium chloride. Sea water contains about 2·5% common salt. The common salt of commerce is obtained from natural brine or from that prepared artificially by pumping water into deposits of rock salt, by evaporation in shallow iron pans or in vacuum evaporators. It is obtained in tropical countries by evaporating sea water by the heat of the sun—the mother liquor, called *bittern*, is an important source for bromine and magnesium from sea-water.

There are many rich salt deposits in India, e.g., Khewra salt mines in the Punjab, and Sambar salt lakes in Rajputana.

The crude salt contains calcium and magnesium chlorides which render it *hygroscopic*. **Pure sodium chloride** is made by passing hydrochloric acid gas into a saturated solution of the impure salt, when pure salt is precipitated; this is filtered, washed with concentrated hydrochloric acid, dried, and then ignited in a platinum dish to remove moisture and hydrogen chloride.

Pure sodium chloride is a transparent, *non-hygroscopic*, crystalline solid which melts at 801°, and readily dissolves in water—35·7 gms. in 100 gms. of water at 0°.

It is the principal source for the manufacture of sodium and chlorine and their compounds, such as HCl, NaCl, NaOH, Na_2CO_3, NaOCl, $NaClO_3$, Na_2SO_4, etc. It is also used for 'salt-glazing' of earthware, and in salting out soap, and in regenerating water-softeners.

Sodium Nitrate, Chile salt petre, $NaNO_3$, occurs in the *caliche* deposits in Chile. The crude caliche, containing up to 65% of sodium nitrate, and about 0·2% sodium iodate, is purified by lixiviation with hot water and crystallisation, yielding a product of 95% purity—the mother liquor, containing *sodium iodate*, is an important source of iodine.

It is a white, crystalline, *deliquescent solid*, very soluble in water. It melts at 316° and decomposes at higher temperature, yielding oxygen: $2NaNO_3 = 2NaNO_2 + O_2$.

It is used as a fertiliser, and in the preparation of sodium nitrite, potassium nitrate and nitric acid.

Sodium sulphate, Na_2SO_4, is prepared in the first step of the Leblanc process by heating common salt with sulphuric acid. The salt-cake formed (p. 401) is dissolved in water—below 32° the decahydrate, $Na_2SO_4, 10H_2O$, called **Glauber's salt,** crystallises out from the aqueous solution; above 32° the anhydrous salt separates and becomes less soluble with the rise of temperature. The decahydrate effloresces in air, yielding the anhydrous salt.

Sodium sulphate is made by Hargreaves process by passing SO_2 from pyrites burner, air and water vapour over heated common salt.

$$4NaCl + 2SO_2 + 2H_2O + O_2 = 2Na_2SO_4 + 4HCl.$$

Synthetic salt cake for use in Kraft paper is made by melting sulphur with soda ash. $2Na_2CO_3 + 2S + 3O_2 = 2Na_2SO_4 + 2CO_2$.

Glauber's salt is used in medicine as a purgative; the anhydrous salt is used in glass-making. Salt-cake is used in making Kraft paper.

Sodium sulphide, Na_2S, is prepared by reducing sodium sulphate with coke at 1000°; $Na_2SO_4 + 4C = Na_2S + 4CO$. It is used in textile industries, in making dyes, and in the extraction of silver.

Detection of sodium.—(i) Sodium compounds give a golden yellow flame, and hence may be detected by *flame test.*

(ii) Zinc uranyl acetate gives a yellow precipitate of sodium zinc uranyl acetate in neutral solution. Magnesium uranyl acetate also gives a similar precipitate.

Potassium K = 39.10

Occurrence.—Potassium is too chemically reactive to be found in the free state. Its compounds are widely distributed in nature, though less abundantly than sodium; thus it is found in plants, in sea-water, in the soil, and in rocks. The sources of potassium compounds are: (i) **The salt deposits in Stassfurt** in Germany, where occurs an extensive potash bed, lying at a depth of about 1000 ft., and containing three layers of potassium salt: **carnallite,** $KCl, MgCl_2, 6H_2O$; **polyhalite,** $K_2SO_4, MgSO_4, 2CaSO_4, 2H_2O$, and **kainite,** $KCl, MgSO_4, 3H_2O$. Nearly all potassium of commerce is obtained from carnallite. (ii)**Brines from the Dead Sea** and from certain drying lakes near Tunis and in California, are commercially exploited to obtain potassium chloride, (iii) **Pot-ash.** The ashes of plants are rich in potassium carbonate and were formerly extracted by lixivation, and used under the name *pot-ash.* The ashes of sea weeds, waste wood, fermented beet sugar molasses residues, and raw wool washings, and the fluedust in blast furnaces and cement kilns, were used as subsidiary sources of potassium compound during the European War of 1914—18, when carnallite was not available to the Allies. Potassium carbonate is extracted from the ash of sunflower stalks in Russia. Grape juice deposits potassium hydrogen tartrate as **cream of tartar.** (iv) **Potash felspar,** or **orthoclase.** $K_2O. Al_2O_3, 6SiO_2$, (v) **Saltpetre or nitre,** KNO_3. It occurs in the soils of the rainless districts of Upper India.

Preparation.—Potassium was formerly made by heating potassium carbonate with charcoal at a white heat: $K_2CO_3 + 2C = 2K + 3CO$, and rapidly cooling the potassium vapour—explosive potassium carbonyl $K_6(CO)_6$ is liable to be formed, if the cooling is slow.

It is now obtained by the electrolysis of fused potassium chloride (Downs cell) or caustic potash (Castner process).

Potassium very closely resembles sodium in properties though it is distinctly more reactive. Thus potassium violently attacks water with the liberation of hydrogen which invariably catches fire and burns with a violet flame. Potassium is feebly radioactive.

Potassium is used in making potassium cyanide. Potassium amalgam is a reducing agent. The liquid alloy of sodium and potassium is used in high temperature thermometers.

Compounds of potassium

Potassium monoxide, K_2O, prepared by heating potassium with potassium nitrate: $2KNO_3 + 10K = 6K_2O + N_2$. It dissolves in water, yielding potassium hydroxide.

Potassium dioxide, KO_2, is obtained as a yellow powder by burning potassium in air or oxygen. It reacts with cold water, giving H_2O_2 which rapidly decomposes into water and oxygen:

$$2KO_2 + 2H_2O = 2KOH + O_2 + H_2O_2.$$

Potassium hydroxide, caustic potash, KOH, is made by the electrolysis of potassium chloride solution. Its m.p. is 360·4°. It resembles sodium hydroxide in properties, but is a stronger base, and more soluble in water—97 gms. in 100 gms. of water at 0°.

Potassium hydroxide is less frequently used as a reagent, since the cheaper caustic soda often serves the purpose. But *in the absorption of carbon dioxide, caustic potash is preferred to caustic soda,* since the $KHCO_3$ formed after sufficient absorption is soluble, while $NaHCO_3$ is insoluble and may, therefore, choke the tubes. Caustic potash is used in making soft soap.

Potassium carbonate, pearl ash, K_2CO_3, was formerly made, under the name **pot-ash,** by extracting wood ashes with water, evaporating the solution to dryness, and then calcinating the residue in pots.

It is now made from potassium chloride by **Precht's process** by passing CO_2 into a concentrated solution of the chloride, containing hydrated magnesium carbonate in suspension at 20°C when an insoluble potassium hydrogen magnesium carbonate is precipitated.

$$2KCl + 3(MgCO_3,3H_2O) + CO_2 = 2(MgCO_3,KHCO_3,4H_2O) + MgCl_2.$$

The precipitate is separated by filtration, and then decomposed either by heating with water under pressure at 140° or by the action of magnesium oxide below 20°.

$$2(MgCO_3, KHCO_3, 4H_2O) = 2MgCO_3 + K_2CO_3 + 9H_2O + CO_2.$$

$$2(MgCO_3, KHCO_3, 4H_2O) + MgO = 3(MgCO_3,3H_2O) + K_2CO_3.$$

The precipitated magnesium carbonate is filtered off for use in the process again, and the filtrate is crystallised for potassium carbonate.

Potassium carbonate may be made by Leblanc process; but the Solvay process cannot be employed, since potassium bicarbonate is soluble in water.

Potassium carbonate is a white, deliquescent solid, m.p. 900°C; a mixture of potassium and sodium carbonates **(fusion mixture)** melts at 712°. Potassium carbonate resembles sodium carbonate in properties, but is more alkaline and more soluble than sodium carbonate.

Potassium bicarbonate is made by absorbing CO_2 in moist potassium carbonate, and then drying the product in a porous plate. The bicarbonate yields *pure potassium carbonate* on gentle heating.

$$K_2CO_3 + H_2O + CO_2 \rightleftharpoons 2KHCO_3.$$

Potassium carbonate is used in the manufacture of glass, soft soap, potassium bromide and iodide, etc. Fusion mixture is used in the laboratory.

Potassium chloride, KCl, occurs in the Strassfurt deposits as *sylvine,* KCl, and as *carnallite,* $KCl,MgCl_2,6H_2O$. Potassium chloride is made by dissolving the carnallite in hot water, and then cooling the solution; potassium chloride crystallises out, whereas the more soluble magnesium chloride remains in solution. The mother liquor is used to treat a fresh supply of carnallite. The mother liquor from carnallite is a source for bromine (p. 269).

KCl is also prepared from fused carnallite—nearly pure KCl separates from the melt, leaving fused $MgCl_2$ behind:

$$KCl,MgCl_2,6H_2O = KCl + MgCl_2,6H_2O.$$

Potassium chloride is a colourless crystalline solid, soluble in water, m.p. 790°. It is used as a fertiliser, and in the manufacture of potassium and other potassium compounds, such as caustic potash, potassium carbonate, potassium chlorate, and potassium dichromate.

Potassium nitrate, KNO_3, also known as *nitre* or *salt petre,* occurs in the soils of tropical countries like India and Ceylon.

It is formed by the bacterial oxidation of decayed nitrogenous organic matter in contact with alkali in the soil. It may be extracted from soils enriched with animal excrements. The process was formely carried out artificially in *'nitre plantations'* in India. Heaps of manure together with lime and wood ashes were interlaid with brush wood for aeration, and left exposed to the air for long period, and occasionally watered with crude sewage. The decay of organic matter produces ammonia, which is converted by bacterial oxidation to nitric acid, and finally to nitrate in the soil. On extracting the soil with water and evaporating the solution crude nitre separates, which is purified by crystallisation.

Potassium nitrate is now manufactured from potassium chloride by double decomposition with sodium nitrate.

$$KCl + NaNO_3 = NaCl + KNO_3.$$

A saturated solution of sodium nitrate is mixed with an equivalent amount of potassium chloride and concentrated by boiling to a density of 1·5, when sodium chloride, being less soluble in the hot solution that any of the other salts, separates out, and is filtered off. On cooling the filtrate, potassium nitrate crystallises out.

Potassium nitrate is a colourless crystalline solid which resembles sodium nitrate, but is less soluble and *is not deliquescent.* It melts at 336° but decomposes at a bright red heat, yielding oxygen: $2KNO_3 = 2KNO_2 + O_2$. Fused potassium nitrate is a powerful oxidising agent.

It is used as a fertiliser; for pickling meat; as a constituent of fireworks and gunpowder, for which the hygroscopic nature of sodium nitrate makes it unsuitable.

Gunpowder is a mixture of about 75% nitre, 10% sulphur and 15% wood charcoal; the ingredients are finely ground and intimately mixed while slightly moist—the paste is pressed between rollers and finally dried. It is exploded by shock or heat at 300°; the products of explosion are gaseous CO_2, CO and N_2, and solid K_2S, K_2SO_4 and K_2CO_3 which produce the smoke. Gunpowder is a safe explosive but is only one-fifth as powerful as dynamite.

$$4KNO_3+5C = 2K_2CO_3+2N_2+3CO_2\,;\quad 2KNO_3+3C = K_2CO_3+CO_2+CO+N_2.$$

$$2KNO_3+S+3C = K_2S+N_2+3CO_2\,;\quad 2KNO_3+S+C = K_2SO_4+N_2+CO_2.$$

Potassium sulphate, K_2SO_4, occurs in Strassfurt potash beds as *schonite,* $K_2SO_4{,}MgSO_4{,}6H_2O$, and *kainite,* $KCl{,}MgSO_4{,}3H_2O$ from which it is obtained by solution and crystallisation. It may be made by neutralising potassium hydroxide or carbonate with dilute H_2SO_4 and concentrating the solution, when anhydrous potassium sulphate crystallises out, m.p. 1050°. It is made in small amounts by heating potassium chloride with concentrated H_2SO_4.

It is used as a fertiliser, particularly in corn and tobacco fields, and in the preparation of potash alum.

Potassium sulphide, K_2S, may be made by heating potassium sulphate with coke. Na_2S and K_2S may also be obtained by reducing the heated sulphates with hydrogen.

Detection of potassium—(i) Potassium compounds give a *violet flame,* which appears *red* when looked through a blue glass. (ii) Sodium cobaltinitrite gives a yellow precipitate of potassium cobaltinitrite in acetic acid solution. Potassium is quantitatively precipitated from alcoholic solutions as *potassium platinic chloride*, K_2PtCl_6 or as *potassium perchlorate*, $KClO_4$.

Alkali cyanides.—Sodium cyanide, NaCN, is a colourless salt with a bitter almond smell of HCN formed by hydrolysis of the salt by atmospheric moisture.

$$NaCN + H_2O \rightleftharpoons NaOH + HCN.$$

The aqueous solution reacts alkaline for the same reason.

It is made by Castner process. Ammonia is passed over fused sodium at 300—400° in an iron retort: $2NH_3 + 2Na = 2NaNH_2 + H_2$.

The fused sodamide formed is run on to red-hot charcoal, when it reacts to form sodium cyanamide, and then cyanide.

$$2NaNH_2 + C = NNa_2CN + 2H_2; \qquad NNa_2CN + C = 2NaCN.$$

Sodium cyanide is used in large quantities in electroplating and in the metallurgy of gold and silver. It is a reducing agent.

Potassium cyanide, KCN, is made by passing ammonia over a mixture of fused potassium carbonate and carbon; the fused potassium cyanide is decanted and cast in moulds.

$$K_2CO_3 + C + 2NH_3 = 2KCN + 3H_2O.$$

Its properties and uses are similar to those of sodium cyanide. The alkali cyanides are used as reagents in the laboratory—they must be used with caution as they are extremely poisonous.

Exercises

1. Describe the method of extraction of metallic sodium from caustic soda. Mention the uses of the metal. What are its reactions with hydrogen, ammonia, sodium nitrate, and aluminium chloride? *Calcutta* '50.

2. How is caustic soda obtained commercially? Discuss the possibility of alkali manufacture in India. Describe the changes that take place when (*i*) caustic soda solution and (*ii*) ammonium hydroxide solution, are separately added to solutions of copper sulphate, ferric chloride, alum and zinc sulphate. How would you show that caustic soda contains hydrogen? *Patna* '37.

3. How is soda ash manufactured by the Solvay process? What is the advantages of the process? How is sodium carbonate converted to (a) sodium bicarbonate, (b) sodium hydroxide? Why is a solution of washing soda alkaline? *Madras* '46.

4. Discuss the changes that occur when (a) sodium nitrate solution is boiled with caustic soda and zinc dust, (b) soda ash is added to ferric chloride solution. (c) carbon dioxide is bubbled through caustic soda solution, (d) a mixture of saturated solutions of potassium chloride and sodium nitrate is heated to boiling. (e) carbon dioxide is passed into ammoniacal brine, (f) sodium sulphate is heated with chalk and coke, (g) soda-ash is heated with ferric oxide, (h) sodium chloride is electrolysed either in the fused state or in aqueous solution.

5. Give an account of the important industries based on common salt as the starting point.

6. Describe briefly the application of electrolysis in industrial processes, using common salt as a raw material.

7. Explain how you would (i) distinguish between solutions of sodium carbonate and bicarbonate, (ii) detect the presence of carbonate and chloride in commercial caustic soda, (iii) estimate the amount of sodium hydroxide and sodium carbonate in commercial caustic soda.

8. How is potassium carbonate manufactured by the Precht's process? Explain why potassium carbonate cannot be prepared by Solvay process. *Punjab* '46.

9. Describe the Ammonia-Soda process of manufacture of sodium carbonate. What is the difference between sodium carbonate and sodium bicarbonate? Why do their solutions react alkaline? What happens when they are heated? How is sodium carbonate converted into caustic soda? Compare their properties. *Calcutta* '46.

10. How is the electrolysis of brine carried out on a large scale? What products are formed by this method?

Describe briefly how you would prepare: (i) solid sodium hydroxide, (ii) hydrochloric acid, (iii) a solution of sodium hyprochlorite from these products?

XXVIII

THE ALKALINE EARTH METALS

The name earth was given by the older chemists to all substances that remained unchanged by fire. Lime, magnesia, strontia, and baryta were found to have alkaline reaction, and were called *alkaline earths*. The alkaline earth metals include magnesium, calcium, strontium and barium. Their physical properties are :

Element	Atomic no.	At. wt.	At. vol.	Density	M. pt. °C	B. pt. °C
Magnesium	12	24·32	13·97	1·74	651	1100
Calcium	20	40·08	25·9	1·55	851	1439
Strontium	38	87·63	34·5	2·54	800	1366
Barium	56	137·36	36·7	3·78	710	1537

General Characteristics.— The general chemistry of the metals of the alkaline earths, Mg, Ca, Sr and Ba, resembles that of the alkali metals, which immediately precede them in the periodic table; but they are somewhat less reactive.

They are 'light metals' but all are denser than water; their melting and boiling points are much higher than those of the alkali metals.

They form bivalent colourless ions, and are strongly electro-positive, being second only to the alkali metals in this respect—the electro-positiveness, and so also the chemical reactivity, increases, as in the alkali metals, with increasing atomic weight.

The chemical relationship of the triad Ca, Sr and Ba is very close. Silver white metals, they quickly tarnish in air. They readily decompose cold water, though less vigorously than the alkali metals, and easily react with acids. They yield the typical basic oxides and true peroxides of the types CaO and CaO, respectively; their oxides lime, strontia, and baryta, are strongly basic, and their hydroxides are alkaline in reaction; but they are weaker bases than the alkalis themselves—their solubility and basic property *increase* with rise of atomic weight. The hydroxides are decomposed by heat. They unite directly with hydrogen and with nitrogen, yielding the hydrides and nitrides respectively.

Their salts are stable, and are not hydrolysed by water—their bicarbonates are known in solution only. Unlike the salts of the alkali metals which are mostly freely soluble, many of the salts of the alkaline earth metals are insoluble in water, *e.g.*, fluorides, sulphates, phosphates and carbonates—the solubility *decreasing* with rise of atomic weight. The nitrates and halides (except fluoride) are soluble in water.

The carbonate are decomposed by strong heat—ease of decomposition *decreasing* with rise of atomic weight.

Their salts impart characteristic colours to the Bunsen flame : calcium, brick-red; strontium, crimson; barium, apple-green.

In certain respects the chemistry of magnesium is more like that of zinc than of calcium. Thus (i) calcium quickly tarnishes in air, while zinc and magnesium tarnish but slowly in air : (ii) calcium decomposes cold water, while zinc and magnesium react with water only at higher temperature; (iii) calcium unites directly with hydrogen, forming the salt-like hydride CaH_2, whereas zinc and magnesium do not form hydrides; (iv) zinc and magnesium form the isomorphous salts, $ZnSO_4$, $7H_2O$ and $MgSO_4$, $7H_2O$, and the double salts of the type, K_2SO_4, $ZnSO_4$, $6H_2O$ and K_2SO_4 $MgSO_4$, $6H_2O$. Calcium sulphate crystallises as $CaSO_4$, $2H_2O$ and does not form any double salts like zinc and magnesium; (v) The salts of zinc and magnesium are readily hydrolysed, while the calcium salts are quite stable towards water.

Calcium and magnesium, on the other hand, unite directly with nitrogen to form nitrides; but this property is not shared by zinc.

Magnesium

Occurrence.—Magnesium is not found free in nature. Its two important minerals are *magnesite*, $MgCO_3$, and *dolomite*, $MgCO_3$, $CaCO_3$. The Stassfurt salt deposits contain the commercially important minerals, *kieserite*, $MgSO_4$, H_2O; *carnallite*, KCl, $MgCl_2$, $6H_2O$; and *kainite*, $MgSO_4$, KCl, $3H_2O$. Magnesium salts are found in mineral springs, in natural brines, and in sea and river waters. It occurs in the minerals, *olivine*, $(Mg, Fe)_2 SiO_4$; *serpentine*, 3MgO, $2SiO_2$, $2H_2O$; *talc*, 3MgO, $4SiO_2$, H_2O; *asbestos*, $CaMg_3(SiO_3)_4$; and *spinel*, MgO, Al_2O_3. Magnesium is a constituent of chlorophyll, the green colouring matter of plants.

Extraction.—Magnesium is prepared commercially in two ways: (i) **The electrolytic method.** —Magnesium is obtained by the electrolysis of a fused mixture of *anhydrous* magnesium chloride and sodium chloride—the latter being added to lower the melting point of magnesium chloride.

The electrolysis is carried out in a covered rectangular iron pot (fig. 167) which acts as the cathode, the anode is a graphite rod, enclosed in a porcelain tube and inserted in the centre of the melt which is kept at 700°. During electrolysis, chlorine evolves at the anode and is led away through the porcelain tube, and magnesium (m. p. 651°) is liberated at the cathode—the liquid metal floats on the surface of the melt and is run off. Since magnesium readily combines with oxygen and nitrogen, the *air within the pot is displaced by a current of hydrogen or coal gas.* The voltage is about 6 volts.

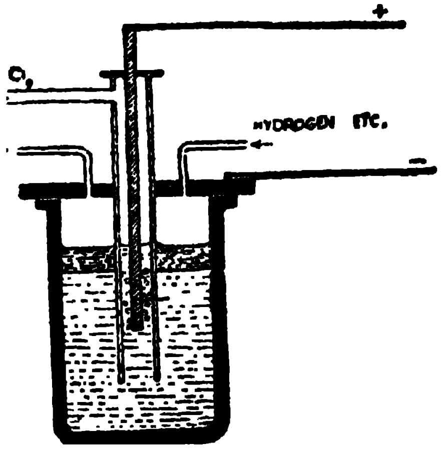


Fig. 167

Magnesium chloride is obtained as the hexahydrate, $MgCl_2$, $6H_2O$, from *carnallite*, and from mother liquors of natural *brines*. It is also extracted from *sea water* by the addition of milk of lime—the precipitated magnesium hydroxide is dissolved in 10% HCl—the solution on concentration yields $MgCl_2$, $6H_2O$. One ton of magnesium is obtained from 800 tons of sea water.

$$MgCl_2 \text{ (in sea water)} + Ca(OH)_2 = Mg(OH)_2 + CaCl_2.$$

The hexahydrate is dehydrated to $MgCl_2$, H_2O which is then rendered anhydrous by heating in a current of hydrogen chloride gas to prevent the formation of an oxy-chloride. Anhydrous $MgCl_2$ is also made by heating a mixture of magnesium oxide (calcined magnesite) and coke in chlorine at 1000°.

$$MgO + C + Cl_2 = MgCl_2 + CO.$$

(ii) **The reduction method.**— A recent development in the production of magnesium is the direct reduction of magnesium oxide by coke :

$$MgO + C \rightleftharpoons Mg + CO.$$

The raw materials, magnesium oxide (produced by the calcination of magnesite) and coke, are briquetted with an oil or pitch binder, and heated to a temperature of about 2000° in a closed electric furnace. The magnesium vapour and carbon monoxide, as they leave the furnace, are *quickly cooled* to about 200° by dilution with a large volume of hydrogen or natural gas in order to prevent the re-oxidation of magnesium during condensation. The magnesium condenses in the form of a powder, which is collected and heated to about 800° in a second electric furnace operated under high vacuum—magnesium volatilises and is condensed out, remelted, and cast into ingots.

Reduction with ferrosilicon takes place at about 1200°. and calcined dolomite can be employed. The operation is carried out under high vacuum. Magnesium volatilises and condenses in a high state of purity.

$$2MgO + CaO + Si = 2Mg + CaSiO_3.$$

Properties of magnesium.— (a) Magnesium is a light, white metal with a bright lustre which tarnishes in moist air due to the deposition of a film of oxide. Soft, malleable, and ductile, it can be readily drawn into wire or ribbon.

(ii) When heated in air or oxygen, magnesium burns with a blinding white flash, which is rich in actinic rays.

(iii) Heated magnesium absorbs nitrogen, yielding magnesium nitride. Combustion of magnesium in air produces a mixture of magnesium oxide and nitride.

$$2Mg + O_2 = 2MgO ; \quad 3Mg + N_2 = Mg_3N_2.$$

(iv) Magnesium powder decompose boiling water, liberating hydrogen ; the heated metal burns in steam: $Mg + H_2O = MgO + H_2$.

(v) It dissolves in dilute acids, including nitric acid, liberating hydrogen, but not in alkalis. $Mg + 2HNO_3 = Mg(NO_3)_2 + H_2$. The metal dissolves in salt solutions rendered acid by hydrolysis:

$$2FeCl_3 + 3Mg + 6H_2O = 2Fe(OH)_3 + 3MgCl_2 + 3H_2.$$

(vi) It is a powerful reducing agent; the heated metal reduces such stable oxides as silica, sodium oxide and potassium oxide. Burning magnesium continues to burn in carbon dioxide, depositing carbon: $2Mg + CO_2 = 2MgO + C$.

(vii) Heated magnesium burns in chlorine, forming magnesium chloride. $Mg + Cl_2 = MgCl_2$. Magnesium does not form any hydride

Uses of magnesium.— It is used (i) in flash light powders (magnesium powder mixed with potassium chlorate or barium peroxide) for photography, in military star shells, in light signals and in fire works; (ii) in the production of light alloys, such as *magnelium* (Al 98 : Mg 2; density 2) and *electron* (Mg 95 : Zn 4·5; Cu 0·5; density 1·8) used in the construction of airships and motorcars; and (iii) as a reducing agent in the laboratory.

Compounds of magnesium

Magnesium oxide, MgO, also called *magnesia,* is made by heating native magnesite: $MgCO_3 = MgO + CO_2$.

It is a white powder with a high m.p. of 2850°. A basic oxide. it dissolves in acids, producing salt and water. It is very slightly soluble in water, importing an alkaline reaction to the solution.

It is chiefly used in the manufacture of *refractory bricks* for furnace linings. A mixture of magnesia and asbestos is used as a 'lagging' for steam pipes to retard the loss of heat by radiation. It is a component of Sorel's cement. It is also used in medicine, since it neutralises acidity in the stomach.

Magnesium hydroxide, $Mg(OH)_2$ is thrown as a white precipitate by adding caustic soda solution to a solution of magnesium sulphate or chloride: $MgSO_4 + 2NaOH = Na_2SO_4 + Mg(OH)_2$.

The precipitate is filtered, washed, and dried at 100°, since it is converted to oxide by heat. It is slightly soluble in water, imparting it an alkaline reaction. It *dissolves in ammonium chloride solution*:

$$Mg(OH)_2 + 2NH_4Cl \rightleftharpoons MgCl_2 + 2NH_4OH.$$

Hence magnesium hydroxide is not precipitated from a solution of magnesium salt by ammonium hydroxide in presence of excess of ammonium chloride.

Magnesium carbonate, $MgCO_3$, occurs in nature as magnesite. It is obtained as a white precipitate by adding sodium bicarbonate to a solution of a magnesium salt; but only basic carbonate, called *magnesia alba*, is precipitated by the addition of sodium carbonate.

Magnesium carbonate dissolves in water containing carbon dioxide, due to the formation of soluble bicarbonate, but is reprecipitated by boiling:

$$MgCO_3 + H_2O + CO_2 \rightleftharpoons Mg(HCO_3)_2.$$

Magnesia alba is used in medicine to neutralise the acidity of the stomach. It is also used in making tooth paste and powders.

Magnesium chloride, $MgCl_2$, may be prepared by dissolving magnesium carbonate in dilute hydrochloric acid and concentrating the solution, when the *hexahydrate*, $MgCl_2, 6H_2O$, crystallises out.

On a commercial scale magnesium chloride is crystallised out from the mother liquors obtained in the preparation of potassium chloride from carnallite (p. 408).

It is a colourless, crystalline, deliquescent solid with a bitter taste, and is exceedingly soluble in water.

It is slightly hydrolysed in solution. The hydrate, $MgCl_2, 6H_2O$, undergoes hydrolysis on being heated in air to about 200°C, evolving steam and hydrogen chloride and yielding magnesium oxychloride, $Mg(OH)Cl$, which decomposes at 600° to magnesium oxide and hydrochloric acid:

$$MgCl_2 + H_2O \rightleftharpoons Mg(OH)Cl + HCl; \quad Mg(OH)Cl \rightleftharpoons MgO + HCl.$$

The hydrochloric acid thus produced attacks iron, and hence sea water cannot be used in marine boilers, since it contains magnesium chloride. The magnesium oxychloride is also formulated as $MgO.MgCl_2$, which on being ignited in air leaves the oxide.

$$2MgCl_2 + H_2O \rightleftharpoons MgO.MgCl_2 + 2HCl.$$
$$2(MgO.MgCl_2) + O_2 = 4MgO + 2Cl_2.$$

Anhydrous magnesium chloride cannot be prepared by heating the hexahydrate, $MgCl_2, 6H_2O$, in air; at 200° it loses 5 molecules of water of crystallisation, and is itself converted to magnesium oxychloride, which finally decomposes into the oxide at 600°, *vide supra.*

The anhydrous salt is prepared (i) by heating the hydrate in vacuum at 175° or in a current of hydrogen chloride; (ii) by heating ammonium magnesium chloride, $MgCl_2$, NH_4Cl, $6H_2O$, prepared by evaporating to dryness a mixed solution of equimolecular amounts of magnesium chloride and ammonium chloride:

$$MgCl_2,NH_4Cl,6H_2O = MgCl_2+NH_4Cl+6H_2O.$$

(iii) by heating to redness a mixture of magnesium oxide and coke in a current of chlorine: $MgO+C+Cl_2 = MgCl_2+CO.$

A paste of magnesium oxide and magnesium chloride **(Sorel's cement)** sets to hard mass on standing; the paste is used for cementing glass and porcelain, as a dental-filling, and as a finish for plaster. Magnesium chloride is also used in dressing cotton threads for spinning.

Magnesium nitrate is made by dissolving oxide or carbonate in dilute nitric acid; it separates from solutions in deliquescent crystals. $Mg(NO_3)_2$, $6H_2O$.

Magnesium sulphate, $MgSO_4$, is found in certain mineral springs, e.g. those at Bath and Epsom. It is mainly obtained commercially by dissolving *kieserite,* $MgSO_4$, H_2O, (practically insoluble in cold water) in boiling water, and then crystallising the solution, when the hepta hydrate, **Epsom salt,** $MgSO_4$, $7H_2O$, separates. It may also be obtained (i) by dissolving magnesite in hot dilute sulphuric acid, (ii) by dissolving dolomite in hot dilute sulphuric acid and removing the insoluble calcium sulphate by filtration.

$$MgCO_3+H_2SO_4 = MgSO_4+H_2O+CO_2.$$

It is a colourless, crystalline solid, soluble in water, and isomorphous with zinc sulphate, $ZnSO_4$, $7H_2O$. A variety isomorphous with $FeSO_4$, $7H_2O$ also exists.

It readily forms double salts with alkali metals, e.g., K_2SO_4, $MgSO_4$, $6H_2O$. The hydrate is rendered anhydrous by heat at 200°.

It is used (i) as a purgative in medicine, (ii) in sizing and loading paper, silk and cotton, (iii) in dyeing and fire-proofing, (iv) in tanning and weighting leather, (iv) as platinised magnesium sulphate in the manufacture of sulphuric acid.

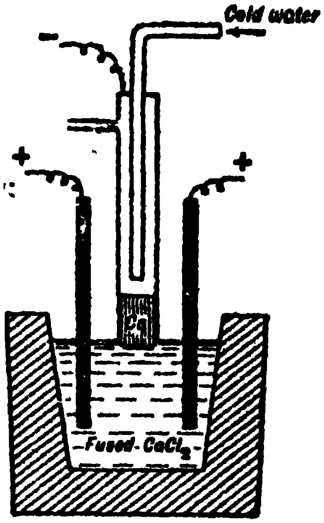
Magnesium sulphide.— MgS, is formed by direct combination. It is hydrolysed by water.

Detection of Magnesium.— (i) Magnesium compounds, mixed with sodium carbonate and heated on charcoal in the oxidising flame, leave a *white incandescent* residue, which on being moistened with cobalt nitrate and heated again, turns *pink,* (ii) Ammonium hydroxide throws from an aqueous solution a white precipitate of magnesium hydroxide, soluble in ammonium chloride solution. (iii) Disodium hydrogen phosphate solution yields a white precipitate of magnesium ammonium phosphate from an ammoniacal solution:

$$MgSO_4 + Na_2HPO_4 + NH_4OH = Mg(NH_4)PO_4 + Na_2SO_4 + H_2O.$$

Calcium

Occurrence.—Calcium is not found free in nature, but in combination with oxygen, it forms about 5%, of the earth's crust. The chief mineral is calcium carbonate, $CaCO_3$, which occurs in two crystalline forms, *aragonite* and *calcite* or *Iceland spur.* Aragonite occurs in the shells of molluscs and in coral. In a massive form calcite occurs as *marble, limestone, and chalk.* Chalk is the shells of marine organisms. Dolomite is the double carbonate $MgCO_3$, $CaCO_3$. Other calcium minerals are: *gypsum,* $CaSO_4$, $2H_2O$; *anhydrite,* $CaSO_4$; *fluorspar,* CaF_2; *apatite,* $CaF_2,3Ca_3(PO_4)_2$ and *lime felspar,* $CaAl_2Si_2O_8$. Calcium is the chief constituent of egg-shells and bones (together with calcium phosphate).



Extraction.—Metallic calcium is obtained by the electrolysis of fused calcium chloride. Calcium chloride (m. p. 774°), mixed with some fluorspar to lower the melting point, is fused at 664° in a graphite crucible (fig. 168). The bath is kept at 700°, which is below the solidification point of calcium, 851°, and above that of the melt, 664°. The anodes are graphite plates, and the cathode is a water-cooled iron rod which just touches the melt. During electrolysis chlorine is liberated at the anodes, and calcium at the cathode, which quickly solidifies. As the calcium accumulates, the cathode is slowly raised by an electrically driven mechanism, so that the metal is produced in the form of a rod, which is protected from oxidation by a layer of calcium chloride.

Properties.—(i) A silver white, fairly soft, melleable metal, calcium tarnishes gradually in moist air. It burns in air with a reddish light, yielding a mixture of the oxide and nitride.

$$2Ca+O_2 = 2CaO\ ; \quad 3Ca+N_2 = Ca_3N_2.$$

(ii) It dissolves readily in cold water, liberating hydrogen and forming calcium hydroxide. $Ca+2HOH = Ca(OH)_2+H_2$.

The metal dissolves vigorously in dilute acids.

(iii) The heated metal combines with oxygen to yield calcium oxide, with hydrogen to yield calcium hydride, with nitrogen to yield calcium nitride, with chlorine to yield calcium chloride, and with sulphur to give calcium sulphide. It also combines with carbon, giving calcium carbide, CaC_2, and hence the metal cannot be prepared from the oxide, by reduction with carbon.

$$Ca + H_2 = CaH_2\ ; \quad Ca + Cl_2 = CaCl_2.$$

(iv) It absorbs ammonia gas in the cold with the formation of the compound $Ca(NH_3)_4$.

Uses.— Calcium is used (i) in freeing absolute alcohol from the last traces of water, (ii) in removing the last traces of air from high vacuum, (iii) in the preparation of calcium hydride, (iv) in metal castings as a deoxidant, and (v) in separating argon from nitrogen.

Compounds of Calcium

Calcium oxide, CaO, commonly called **quick lime,** or **lime** is made by decomposing limestone at a high temperature, about 1000° in a lime-kiln, which is a tall brick structure, generally built near a limestone quarry. $CaCO_3 \rightleftharpoons CaO+CO_2 - 42{,}000$ calories. Lumps of limestone are introduced into the kiln through a charging door at the top, and heated either by producer gas admitted at the base or by the combustion of coal (introduced along with limestone) inside the kiln. Lime works its way gradually down the kiln and is withdrawn at the base; carbon dioxide passes out through an exit at the top (fig. 169).

It is a white amorphous powder, which emits intense white light (*lime light*), when heated in the oxy-hydrogen flame. *It fuses at* 2570°. A basic oxide, it reacts with acids and acidic oxides, yielding salts. It reacts with strongly heated silica, forming easily fusible calcium silicate; $CaO + SiO_2 = CaSiO_3$. It reacts with dry CO_2 only above 300°. It reacts with chlorine above 300° giving off oxygen:

$$2CaO + 2Cl_2 = 2CaCl_2 + O_2.$$

When quick lime is sprayed with water much heat is evolved and clouds of steam are given off; lime combines with water, swells up, cracks and finally crumbles to a fine, dry, white powder of calcium hydroxide, $Ca(OH)_2$, called *slaked lime,* $CaO + H_2O = Ca(OH)_2$. The process is called *slaking of lime* and the product *slaked lime.*

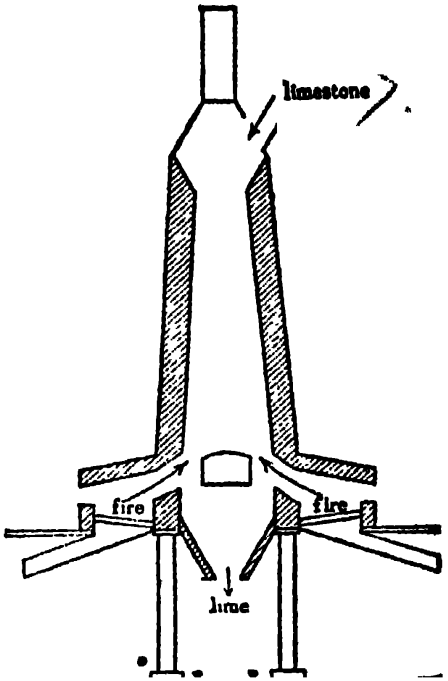


Fig. 169

Calcium hydroxide, slaked lime, $Ca(OH)_2$, is obtained by spraying water on the quick lime. It is sparingly soluble in water, about 0·23 gm. in 100 gms. of water at 0°: *it is less soluble in hot water than in cold.* The solution is called **lime-water**; it readily absorbs carbon dioxide and is used as a test for the gas (p. 324).

A suspension of slaked lime in water is called **milk of lime.** In its reactions it resembles caustic soda, and is largely used in industries as a cheap source of alkali.

Uses of lime.— Quick lime is used as a drying agent; as a basic flux in metallurgy; in the manufacture of calcium carbide; and for producing lime light. Slaked lime is used for the manufacture of caustic soda and bleaching powder; in glass-making and in the recovery of ammonia in the Solvay process; for softening temporary hard water; for the removal of hair from hides in leather industry; for *whitewashing* of buildings; for the purification of coal gas and sugar; in agriculture; in the manufacture of mortar and cement.

Mortar.—Builder's mortar is a mixture of slaked lime (1 part) and sand (3 parts) made into paste with water. It sets to a hard mass, by loss of water, into the bricks; slaked lime is gradually converted to calcium carbonate by absorbing atmospheric carbon dioxide.

Cement.—Portland cement is manufactured by heating finely pulverised limestone with clay at 1400° in an inclined rotary kiln (fig. 170); the charge is fed into the top of a long rotating tubular furnace, which is fired by injecting coal dust and air at the base. The charge sinters, and the resulting *cement clinker* is taken out at the base, cooled, and then ground in tube mills to a fine powder, and packed in air-tight barrels. It is essentially a mixture of tricalcium silicate, $3CaO,SiO_2$, and tricalcium aluminate, $3CaO,Al_2O_3$. It sets with water (whence the name *hydraulic cement*) within a few hours (about 2 to 3% gypsum is added to cement to retard quick setting) to a hard mass, which becomes steadily harder with time. The setting is due to the hydrolysis of calcium silicate and aluminate—the products of hydrolysis forming interlocking crystals.

Ordinary mortar cannot set under water, since its setting requires carbon dioxide; but a paste of cement and sand (cement mortar) sets easily under water.

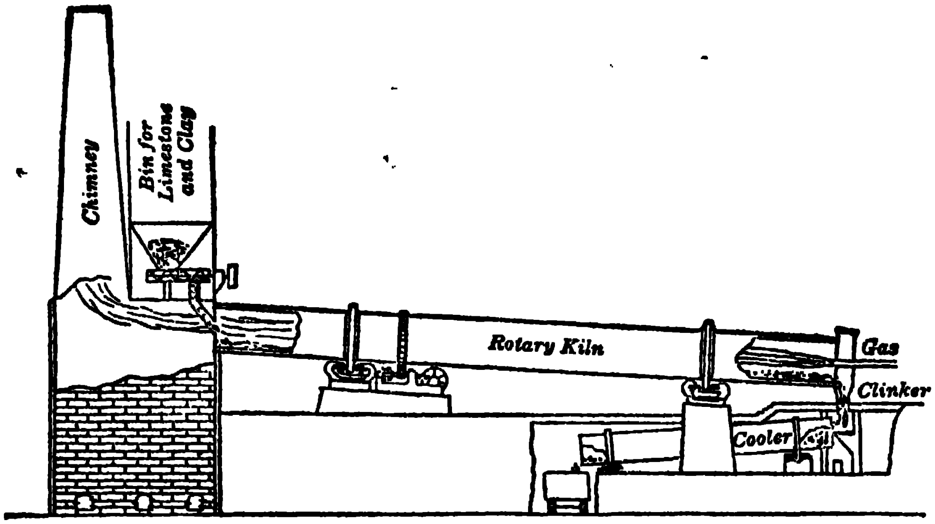


Fig. 170

Concrete is a mixture of cement with sand and stone chips. It set to hard rock-like mass, and is largely used for building purposes. The tensile strength of concrete is increased by allowing it to set on a framework of steel rods; the material thus obtained is called *reinforced concrete*, and is used for the construction of bridges, buildings and embankments,, etc.

Soda lime is a dry mixture of slaked lime and caustic soda, made by slaking lime with strong caustic soda solution. It is used as a drying agent; as an absorbent for acid gases; in *gas masks*.

Calcium carbonate, $CaCO_3$, occurs in nature as marble, limestone, chalk, coral, calcite, etc. It is prepared as a white powder, known as precipitated chalk, by dissolving marble or limestone in hydrochloric acid, and removing any iron and aluminium present, by precipitating with ammonia, and then adding ammonium carbonate to the solution: the precipitate is filtered, washed and dried:

$$CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl.$$

Lime stone finds extensive use in making cement, lime and glass, and as a flux in metallurgy. *Marble* is used in building and sculpture. *Chalk* is used in the preparation of *whiting*, etc. *Precipitated chalk* is used in medicine, and in the preparation of tooth pastes and face powders.

It dissolves in water containing carbon dioxide, forming calcium bicarbonate but is precipitated from the solution by boiling:

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2.$$

Calcium chloride, $CaCl_2$, is produced in huge quantities in the Solvay process. It can be prepared by dissolving the carbonate in hydrochloric acid, and concentrating the solution, when colourless deliquescent crystals of the hexahydrate, $CaCl_2,6H_2O$, are deposited

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

It dissolves in water with a considerable lowering of temperature (the eutectic point is $-55°$) and hence the use of calcium chloride solution in refrigerators. It also dissolves readily in alcohol. The hydrate is rendered (unlike magnesium chloride) anhydrous by heat; the product, however, contains a little lime due to slight hydrolysis:

$$CaCl_2 + H_2O \rightleftharpoons CaO + 2HCl.$$

The pure anhydrous salt (m.p. 782°) is obtained by heating the hydrate in a current of dry hydrogen chloride.

The anhydrous salt is used for drying gases and liquid organic compounds, but cannot be used for drying ammonia or alcohol due to the formation of the compounds, $CaCl_2,8NH_3$ and $CaCl_2, 4C_2H_5OH$; for the preparation of metallic calcium.

Calcium nitrate, $Ca(NO_3)_2$, is prepared by the action of dilute nitric acid upon lime stone. It is slightly deliquescent. It finds some use as a fertiliser.

Calcium sulphate, $CaSO_4$, occurs as *anhydrite*, $CaSO_4$, and as the dihydrate, $CaSO_4,2H_2O$, *gypsum*, *alabaster or satin-spar.* It is sparingly soluble in water, having the maximum solubility of 0·21% at 38°. When gypsum is heated, at about 120° it partially loses water, giving the hemi-hydrate, *plaster of Paris,* $2CaSO_4,H_2O$, which becomes anhydrous by heat at 200°; slight decomposition into calcium oxide and sulphur trioxide occurs above 400°.

Plaster of Paris, $2CaSO_4,H_2O$.—It is made by heating gypsum at about 120°, without any contact with carbonaceous fuel (to prevent reduction into sulphide $CaSO_4 + 4C = CaS + 4CO$), in large steel pots provided with mechanical stirrers or in a rotary kiln. Gypsum partially loses water producing plaster of Paris. The temperature is carefully controlled, since at higher temperature it is fully dehydrated, and is said to be *dead burnt,* as the product then loses its power of quick setting. Plaster of Paris, made into a paste with water, quickly sets to a hard mass, *with a slight expansion in the process*—setting being due to reconversion into gypsum.

$$2((CaSO_4,2H_2O)\ (\text{gypsum}) \rightleftharpoons 2CaSO_4,H_2O\ (\text{plaster of Paris}) + 3H_2O.$$

Plaster of Paris is used in taking casts in moulds; in surgical bandages; as a cement and wall plaster. Gypsum is used in the preparation of plater of Paris and ammonium sulphate; for filling or glazing paper; as a fertiliser in agriculture; in making *crayons*, so-called 'chalk' pencils.

Calcium sulphide, CaS, is formed by reducing calcium sulphate with coke or hydrogen. It was formerly obtained as *alkali-waste* in Leblanc process. It is sparingly soluble in water, in which it is partially hydrolysed.

$$2CaS + 2HOH \rightleftharpoons Ca(OH)_2 + Ca(SH)_2.$$

Impure calcium sulphide becomes phosphorescent after an exposure to sunlight. It is used in tanning for removing hair from hides; and in depilatories.

Detection of calcium.—(i) Calcium compounds may be detected by *flame* test, since they give a *transient* deep red colour, which readily, turns *brick-red,* (ii) Ammonium oxalate throws from an aqueous solution a white crystalline precipitate of calcium oxalate, insoluble in acetic acid.

Strointium and Barium

Occurrence.—The chief minerals of strontium are: *strontianite*, $SrCO_3$, and *celestine*, $SrSO_4$, and those of barium are: *witherite*, $BaCO_3$, and *barytes* or *heavy spar*, $BaSO_4$.

Preparation.—Metallic strontium and barium are prepared by the electrolysis of the fused chloride or by heating the oxide with aluminium powder *in vacuo.*

Properties.—Soft, silver-white, light metals, they burn to their monoxides in air—barium is so reactive that it inflames spontaneously. They decompose cold water—barium reacting more vigorously—with the liberation of hydrogen and forming the hydroxide. They unite, when heated, with hydrogen and nitrogen, yielding respectively hydrides and nitrides which are decomposed by water :

$$BaH_2 + 2H_2O = Ba(OH)_2 + 2H_2; \quad Ba_3N_2 + 6H_2O = 2NH_3 + 3Ba(OH)_2.$$

Oxides.—The oxides are best obtained by heating the nitrate or reducing the carbonate with charcoal at a red heat : $2Sr(NO_3)_2 = 2SrO + 4NO_2 + O_2$: $BaCO_3 + C = BaO + 2CO$. The hydroxide is also converted to the oxide by heat.

White infusible powder, more fusible than quick lime, they are slaked by water to form hydroxides with evolution of much heat. When heated to 500° in air or oxygen barium oxide forms peroxide, BaO_2, which itself decomposes above 800° or under reduced pressure : $2BaO + O_2 \rightleftharpoons 2BaO_2$. Strontium oxide also combines with oxygen under pressure at a dull red heat to form the peroxide, SrO_2.

Hydroxides.—The hydroxides are made by heating the oxides with hot water : $BaO + H_2O = Ba(OH)_2$. The hydroxides are manufactured by heating the carbonates to strong redness in a current of steam : $BaCO_3 + H_2O = Ba(OH)_2 + CO_2$. Native carbonates may be used or the carbonates may be made from mineral sulphates by heating them with carbon to form sulphides, which are then treated with moist carbon dioxide :

$$BaSO_4 + 4C = BaS + 4CO; \quad BaS + H_2O + CO_2 = BaCO_3 + H_2S.$$

Barium hydroxide is known as *baryta*. The hydroxides dissolve in water, giving alkaline solutions—baryta water is strongly alkaline and gives a white precipitate of the carbonate, $BaCO_3$, with carbon dioxide.

Strontium and barium salts.—The carbonates or sulphides are dissolved in acids, and the salts crystallised.

Crystals of strontium chloride, $SrCl_2,6H_2O$, are efflorescent but those of *barium chloride*, $BaCl_2,2H_2O$, are unchanged in the air. *Strontium nitrate*, $Sr(NO_3)_2$, and *barium nitrate*, $Ba(NO_3)_2$, are used in fire works, mixed with charcoal and sulphur to produce *red* and *green fire* respectively.

Native sulphates which are insoluble in acids are converted to : (i) *carbonates* by fusion with excess of sodium carbonate—the carbonates are separated from the sodium sulphate by boiling the fused mass with water and washing; $BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$ or (ii) *sulphides* by strongly heating with carbon : $BaSO_4 + 4C = BaS + 4CO$.

Carbonates.—The carbonates resemble chalk but are more stable towards heat. They are fairly readily converted to oxides, if heated to redness with carbon : $BaCO_3 + C = BaO + 2CO$.

Sulphates.—By adding dilute sulphuric acid or a soluble sulphate to a solution of a barium salt, *barium sulphate* is formed as a fine white precipitate nearly insoluble in water (2·4 mgm. per litre) and acids, except hot concentrated HCl or H_2SO_4. The insolubility of barium sulphate provides a method for the estimation of barium as sulphate.

Barium sulphate is used as a basis for paints under the name *blanc fixe* but has a poor covering power. It is also used as a filler for paper and rubber.

Strontium sulphate resembles barium sulphate, but is more soluble in water (about 0·01 per cent at 15°).

Sulphides.—Barium sulphide is prepared by reducing the sulphate with coke at 1000° : $BaSO_4 + 4C = BaS + 4CO$. It dissolves in water, forming the hydroxide and hydrosulphide : $2BaS + 2H_2O = Ba(OH)_2 + Ba(SH)_2$.

The white pigment **lithopone** is a mixture of a barium sulphate and zinc sulphide made by precipitation by the interaction of solutions of barium sulphide and zinc sulphate and heating the precipitate at 50° ta 60° :

$$BaS + ZnSO_4 = BaSO_4 + ZnS.$$

Strontium sulphide resembles barium sulphide.

Detection.—(i) A strontium compound imparts a *persistent crimson colour* to the Bunsen flame, while a barium compound is characterised by the *green colour of its flame.*

(ii) Potassium chromate gives, with a solution of a barium salt, a yellow precipitate of barium chromate insoluble in acetic acid—strontium chromate is soluble in acetic acid. Ammonium sulphate gives, with a solution of strontium, salt a white precipitate of $SrSO_4$, insoluble in acids.

XXIX

ZINC, CADMIUM & MERCURY

Group IIB of the periodic classification contains the metals zinc, cadmium and mercury.

	Atomic no.	At. wt.	At. vol.	Density	M. pt. °C.	B. pt. °C
Zinc ...	30	65·38	9·21	7·1	419	920
Cadmium ...	48	112·41	13·01	8·64	321	767
Mercury ...	80	200·61	14·02	13·6	—39	356·9

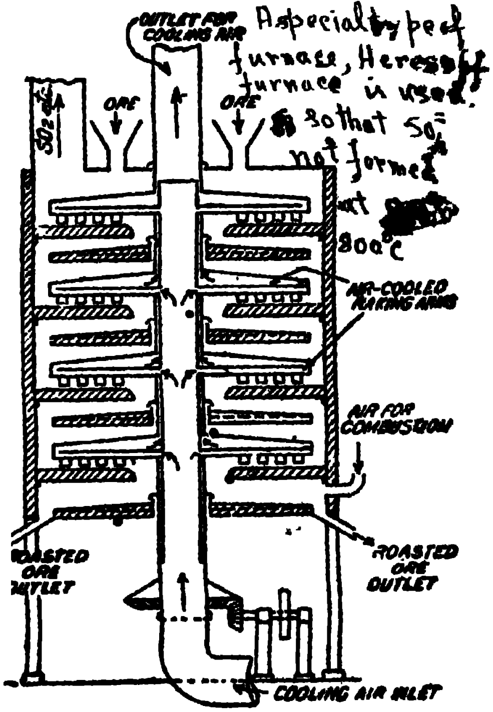
Zinc

Occurrence.– The principal ore of zinc is zinc sulphide or **zinc blende** ("black-jack"), ZnS, which is usually associated with argentiferous *galena*. Less important minerals are: *calamine* (*smithsonite* in the U.S.A.), $ZnCO_3$; *electric calamine* (*calamine* in the U.S.A.), Zn_2SiO_4,H_2O; *willemite* Zn_2SiO_4; *franklinite*, ZnO, Fe_2O_3; and *zincite* or red zinc ore, ZnO.

Extraction.— The most important source of zinc is zinc blende. The mixed ore of blende and galena is concentrated by oil-floatation process. The finely-crushed ore is churned up with water containing eucalyptus oil and a little acid—galena collects in the froth formed on the surface of the liquid, and is removed. The blende collects in a second froth produced by adding more oil and acid to the liquid —the gangue sinks to the bottom. Zinc is obtained from the zinc concentrate either (i) by the *reduction process*, or (ii) by the *electrolytic process.*

(i) **The reduction process.**—It consists of three steps: (a) *roasting*, (b) *smelting*, and (c) *refining*:

(a) **Roasting.**—In order to convert the blende into zinc oxide, the zinc concentrate is roasted in air at a high temperature in a multiple-hearth roaster through which air circulates, and where the blende is raked in a series of shelves (fig. 171). Care is taken that only zinc oxide is produced, and no zinc sulphate, since it would again give sulphide in subsequent reduction. Some sulphate that it always formed is decomposed at the high temperature used.



A special type of furnace, Heresoff furnace is used. so that $SO_4^{=}$ not formed at [illegible] 800°C

Fig. 171

$$2ZnS + 3O_2 = 2ZnO + 2SO_2; \quad ZnS + 2O_2 = ZnSO_4.$$

5[illegible]

$ZnSO_4 + 4C = ZnS + 4CO$

The sulphur dioxide may be utilised in making sulphuric acid. The carbonate ore, if used, is also calcined to eliminate carbon dioxide which readily oxidises zinc vapour :

$$ZnCO_3 = ZnO + CO_2; \quad Zn + CO_2 \rightleftharpoons ZnO + CO.$$

(b) **Smelting.**—The roasted ore (zinc oxide) is then mixed with about half its weight of powdered coke, and packed into fire clay retorts R closed at one end and set in several rows in a furnace, sloping towards the open end (fig. 172)—the open end of each retort is fitted with a conical clay tube C (*condenser*) which in its turn is

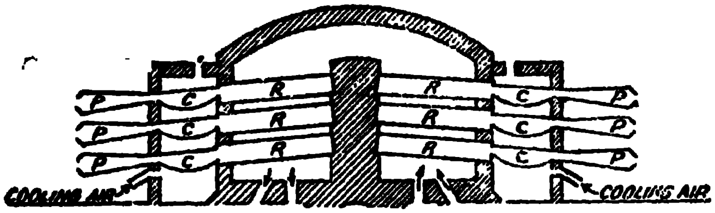


Fig. 172

luted with clay with an iron tube P, known as the prolong. The furnace is heated to 1350° by producer gas and air *on the regenerative principle of heat economy*. The zinc oxide is reduced by coke, yielding carbon monoxide, and metallic zinc (b. pt. 920°) which distils off.

$$ZnO + C = Zn + CO.$$

The zinc vapour passes with the carbon monoxide into the condensing system, where the zinc partly deposits as liquid metal in the condenser and partly as *zinc-dust* in the prolong. The carbon monoxide passes on and burns at the mouth of the condensers.

The first portion of the distillate, collecting as *zinc-dust* in the *prolong*, contains any *cadmium* that may be present in the ore, and some zinc oxide formed by the oxidation of zinc vapour by oxygen or carbon dioxide, initially contained in the condensing system. *Since zinc vapour is readily oxidised by carbon dioxide, the smelting is done in a carbon monoxide atmosphere.*

The molten metal in the condensers is transferred to moulds where it solidifies to give crude zinc, called **spelter,** which contains about 97 to 98 per cent zinc, 2 per cent lead, and traces of iron, cadmium and arsenic.

(c) **Refining.**—The crude zinc is refined by fractional distillation. The molten spelter is fed into a column heated above the boiling point of zinc (920°), when the zinc and cadmium distil out at the top and are condensed, and lead (b.p. 1620°) and iron (b.p. 2800°) collect at the bottom of the column. The molten zinc-cadmium alloy is then similarly treated in a second column heated above the b.p. of cadmium (767°) when the more volatile cadmium distils off at the top and very pure zinc (99·99 per cent) collects at the base of the column. Cadmium is recovered as a by-product. The zinc oxide is also smelted with coal in arc or resistance type electric furnaces.

Continuous vertical retorts are also used. In the vertical retort process the charge of roasted ore (zinc oxide) and coke is fed through a charging door at the top into tall narrow vertical fireclay retorts (fig. 173) fired externally by producer gas and air. The charge gradually descends by gravity and the zinc oxide is reduced to the metal; $ZnO + C = Zn + CO$. The temperature is high enough to vaporise the zinc. The zinc vapour and carbon monoxide, pass out through an exit at the top into a condenser in which the zinc condenses and CO goes out. Producer gas is forced into the retort from below in order to completely drive out the zinc vapour. The residue as it descends down, is automatically withdrawn at the base.

(ii) **Electrolytic method.**— Pure zinc is made by electrolysis of an acidified solution of pure zinc sulphate with a high current density. The zinc concentrate is roasted in air below 700° to convert the blende into zinc sulphate. The roasted mass is leached with dilute sulphuric acid, when an impure solution of zinc sulphate is obtained. The solution is treated with milk of lime to precipitate iron and aluminium as hydroxides, and silica as calcium silicate, which are filtered off. The filtrate is then stirred with zinc-dust to precipitate the more noble metals copper and cadmium which are removed by filtration. The solution is next acidified and electrolysed with a lead anode and aluminium cathode—the zinc deposited on the cathode is stripped off; it is of 99·95% purity.

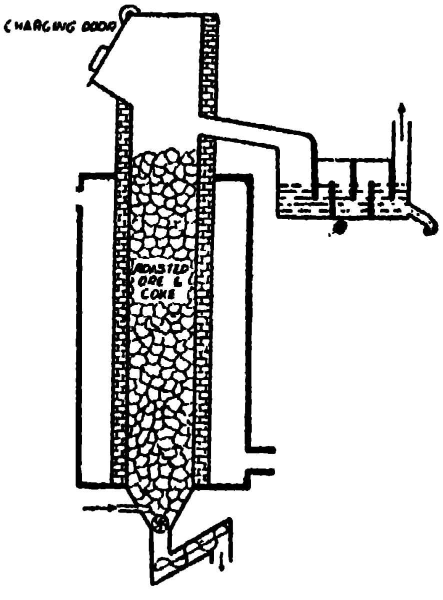


Fig. 173

Properties of zinc.— (i) Zinc is a bluish-white metal, which tarnishes in moist air by the formation of film of basic carbonate.

Though brittle below 100° and above 200°, commercial zinc is malleable and ductile between 100° and 150°, at which temperature it can be rolled into sheets and drawn into wire. Pure zinc is malleable at all temperatures.

Zinc burns in air with a green flame if strongly heated, forming white clouds of zinc oxide which settle in wooly flocks (*philosopher's wool*): $2Zn + O_2 = 2ZnO$.

(ii) Pure zinc is not attacked by water; commercial zinc, also zinc coated with copper, decomposes boiling water, giving off hydrogen. The red-hot metal reacts vigorously with steam, producing hydrogen.

$$H_2O + Zn = H_2 + ZnO.$$

(iii) Commercial zinc readily dissolves in HCl and dil. H_2SO_4, yielding hydrogen; very pure zinc dissolves only exceedingly slowly. The metal is a convenient reducing agent in presence of dilute sulphuric acid: $Fe_2(SO_4)_3 + Zn = ZnSO_4 + 2FeSO_4$.

Zinc dissolves in nitric acid (p. 250). Zinc reacts with hot concentrated sulphuric acid, giving off SO_2:

$$Zn + 2H_2SO_4 = ZnSO_4 + 2H_2O + SO_2.$$

(i) It dissolves in hot solutions of caustic soda and potash, yielding hydrogen and zincate. $Zn + 2NaOH = Na_2ZnO_2 + H_2$.

A mixture of zinc dust and caustic soda reduces an aqueous solution of a nitrate to ammonia.

$$NaNO_3 + 4Zn + 7NaOH = NH_3 + 4Na_2ZnO_2 + 2H_2O.$$

(v) It combines with chlorine if heated, yielding zinc chloride; but it does not directly combine with hydrogen, nitrogen or carbon. Zinc nitride is formed by heating the metal in ammonia.

$$3Zn + 2NH_3 = Zn_3N_2 + 3H_2.$$

(vi) It precipitates the more noble metals, such as lead, copper, silver and gold, from their aqueous solutions.

$$CuSO_4 + Zn = ZnSO_4 + Cu.$$

Uses of zinc.— (i) Remarkably resistant to atmospheric corrosion, zinc is largely used to protect iron from rusting. The **iron sheets or ware** are cleaned by a sand-blast followed by 'pickling' with dilute hydrochloric acid, and then dipped in molten zinc containing a flux of ammonium chloride, when a thin adherent coating of zinc is formed; the process is called **galvanisation** and the product *galvanized iron.* Iron articles may also be coated with zinc by heating them in zinc dust **(sherardizing)**, by spraying, or by electro-deposition. Galvanised iron is not used for food stuff containers, since zinc is poisonous.

(ii) Zinc is used for the manufacture of *zinc white,* and several useful alloys such as *brass* and *German-silver;* for the precipitation of gold and silver in the cyanide method; for the desilverisation of lead in Parkes process; and as the anode material in galvanic cells.

(iii) Zinc dust or granulated zinc an important reducing agent. *Zinc dust,* containing finely divided zinc with some zinc oxide, is made by atomising molten zinc with a jet of high pressure air; also found in the *prolong* during the smelting process. *Granulated zinc* having a large surface for a given weight, is prepared by pouring a thin stream of molten zinc in water.

Compounds of Zinc

Zinc oxide, ZnO, is made for use as the pigment **zinc white** by burning zinc in a current of air, the oxide collecting in white wooly flocks, known as *philosopher's wool*: $2Zn + O_2 = 2ZnO$. It is made for preparing zinc *ointment* in pharmacy, by precipitating solution of zinc sulphate with sodium carbonate and heating the basic carbonate.

An insoluble white powder, it turns yellow on heating, the white colour appearing on cooling. It is amphoteric (p. 176). It is reduced to metal by carbon or hydrogen at a red heat. On being heated with cobalt nitrate, it yields the green pigment cobalt zincate, $CoZnO_2$, called *Rinman's green.* Zinc oxide is used as an absorbent in surgical dressing, and as a 'filler' for rubber.

Zinc hydroxide, $Zn(OH)_2$, is thrown as a white gelatinous precipitate by adding the correct amount (not in excess) of caustic soda to a solution of a zinc salt—the precipitate is soluble in excess of the alkali, forming zincate.

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4;$$
$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O.$$

It also dissolves in ammonium hydroxide, forming the colourless complex hydroxide, $[Zn(NH_3)_4](OH)_2$. It may be precipitated from solutions of zinc salts by ammonia (not in excess), but *not by ammonia containing ammonium chloride.* Zinc hydroxide is an amphoteric compound like zinc oxide.

Zinc carbonate, $ZnCO_3$, is precipitated as an insoluble white powder by adding sodium bicarbonate to a solution of a zinc salt—sodium carbonate yields a basic carbonate. It loses carbon dioxide by gentle heat, leaving a residue of zinc oxide.

Zinc chloride, $ZnCl_2$, is obtained in solution by dissolving metallic zinc, the oxide or the carbonate in hydrochloric acid—the solution on evaporation yields the crystals of the monohydrate, $ZnCl_2,H_2O$; but this cannot be rendered anhydrous by heat, since a basic chloride is formed:

$$ZnCl_2 + HOH \rightleftharpoons Zn(OH)Cl + HCl.$$

$$2ZnCl_2 + H_2O \rightleftharpoons ZnCl_2.ZnO + 2HCl.$$

Anhydrous zinc chloride is obtained (i) by heating the hydrate, $ZnCl_2,H_2O$ in a current of hydrogen chloride, (ii) by passing hydrogen chloride over heated zinc, (iii) by passing chlorine over heated zinc or zinc oxide. $2ZnO+2Cl_2 = 2ZnCl_2 + O_2$. It is fused and cast into sticks. Zinc chloride is highly deliquescent and is soluble in water, alcohol, acetone, ether and pyridine.

Zinc chloride is used as a dehydrating agent and as a catalyst in organic chemistry; as a caustic in surgery; in making *soldering fluids* ('killed spirits'); in the preparation of vulcanised fibre and activated charcoal; in the preservation of timber against 'dry rot; in making dental filling (a paste of zinc chloride with zinc oxide and powdered glass).

Zinc nitrate, $Zn(NO_3)_2$, is obtained in colourless deliquescent crystals, $Zn(NO_3)_2, 6H_2O$, by dissolving zinc carbonate in dilute nitric acid and crystallising the solution.

Zinc sulphate, $ZnSO_4$, is prepared in solution by dissolving metallic zinc, the oxide or the carbonate in dilute sulphuric acid; colourless efflorescent crystals of the heptahydrate, $ZnSO_4,7H_2O$, known as **white vitriol,** deposit on concentrating the solution to crystallisation below 30°.

Industrially blende, ZnS, is converted to zinc sulphate by roasting in air below 700°. The roasted mass is lixiviated with dilute sulphuric acid, and the solution evaporated to crystallisation below 30°, when the crystals of white vitriol separate: $ZnS + 2O_2 = ZnSO_4$.

It is isomorphous with Epsom salt and green vitriol. It forms double salts with potassium or ammonium sulphates, e.g., $K_2SO_4, ZnSO_4, 6H_2O$. The hydrate becomes anhydrous by heat at 450°; it decomposes on further heating, leaving a residue of zinc oxide.

$$2ZnSO_4 = 2ZnO + 2SO_2 + O_2.$$

Zinc sulphate is used in making the white pigment **lithopone** (a mixture of zinc sulphide and barium sulphate made by precipitation : $BaS + ZnSO_4 = BaSO_4 + ZnS$); in solution ($\frac{1}{8}$ per cent, $ZnSO_4$) as an eye lotion; as a mordant in calico printing; in preserving hides.

Zinc sulphide, ZnS, occurs as *blende*, and may be made by heating zinc filings with sulphur. It is obtained as a white precipitate by adding ammonium sulphide to a solution of a zinc salt. It is insoluble in water, alkali and acetic acid, but readily soluble in dilute mineral acids. Hence if hydrogen sulphide is passed into :

(i) an alkaline solution of zinc salt, zinc sulphide is precipitated :

$$Na_2ZnO_2 + 2H_2S = Na_2S + ZnS + 2H_2O;$$

(ii) an acidified (with dilute HCl or H_2SO_4) solution of zinc salt, no precipitate is formed.

(iii) a solution of zinc sulphate (or chloride) ZnS is at first precipitated but the precipitation soon stops due to the acid formed. But when sodium acetate is added to the solution, the zinc is completely precipitated since the mineral acid formed is converted into acetic acid in which the ZnS is insoluble.

$$ZnSO_4 + H_2S = ZnS + H_2SO_4$$

$$2CH_3COONa + H_2SO_4 = 2CH_3COOH + Na_2SO_4.$$

In presence of traces of impurities, e.g., bismuth sulphide, zinc sulphide becomes phosphorescent. It is used as a white pigment.

Detection of zinc.— (i) Zinc compounds, on being heated with sodium carbonate on charcoal in blow pipe flame, yields a white incandescent residue (of zinc oxide) which is *yellow when hot*, and *white when cold.* The residue, on being moistened with cobalt nitrate and heated again, turns *green* (*Rinman's green*).

(ii) Ammonium sulphide yields with a solution of a zinc salt, a white precipitate of zinc sulphide insoluble in alkali and acetic acid, but soluble in dilute mineral acids.

(iii) Caustic soda gives with a solution of a zinc salt a white precipitate of zinc hydroxide, soluble in excess of the alkali.

Comparison of Calcium, Magnesium and Zinc.— (i) **Physical properties:** The elements Ca, Mg and Zn are silver-white metals which are good conductors of heat and electricity. Their densities increase, but the m.p.'s and b.p.'s decrease from calcium to zinc.

		Calcium	Magnesium	Zinc
Density	...	1·55	1·74	7·14
Melting point	...	851°C	651°C	419°C
Boiling point	...	1439°C	1110°C	920°C

The metals are fairly *strongly electropositive* but this property gradually decreases from calcium to zinc.

(ii) **Valency:** The metals are uniformly *divalent.*

(iii) **Action of air:** Calcium readily tarnishes in air, while Mg and Zn tarnish but slowly in air. All three metals burn in air: Ca burns to CaO and Ca_3N_2, and Mg to MgO and Mg_3N_2, but zinc to ZnO only.

(iv) **Action of acids:** All three metals dissolve in dilute HCl or H_2SO_4 with the liberation of hydrogen. Magnesium alone gives hydrogen with dilute nitric acid.

(v) **Action of water:** Calcium dissolves in cold water, liberating H_2, Mg powder and Zn-Cu couple decompose boiling water, giving off H_2. Red-hot Mg and Zn readily decompose steam with liberation of hydrogen.

(vi) **Action of hydrogen:** Calcium *alone* forms stable salt-like hydride, CaH_2, by direct absorption of H_2 at about 350°.

(vii) **Action of nitrogen:** Red-hot Ca and Mg (but not Zn) form Ca_3N_2 and Mg_3N_2 by direct absorption of nitrogen.

(viii) **Oxide and hydroxides:** All three metals form very stable oxides of the type MO. CaO and MgO are highly refractory and are used in furnace lining. CaO is not reduced by carbon; MgO can be reduced by carbon at 2000°C, while ZnO is readily reduced by carbon. The oxides are all *white* in colour, and become *incandescent* by strong heat; ZnO alone becomes yellow while hot but white when cold.

CaO is *strongly basic*, MgO is *weakly basic*, and ZnO is *amphoteric*. CaO is *sparingly soluble* in water—slaking of lime with water is highly exothermic. MgO is very *slightly* soluble in water— the solution is alkaline to litmus. ZnO is insoluble in water. Calcium hydroxide is a *strong base*, sparingly soluble in water. $Mg(OH)_2$ is *amphoteric;* insoluble in water, it dissolves in caustic alkalis, NH_4Cl and also in ammonia.

(ix) **Carbonate:** Sodium carbonate solution precipitates the normal carbonate of calcium, namely $CaCO_3$, but only *basic carbonates* of Mg and Zn, showing the *weaker basic character* of MgO and ZnO. The carbonates dissolve (but only slightly in the case of Zn) in carbonic acid to form unstable bicarbonates. The carbonates decompose by heat into the oxide of the metal and CO_2—the ease of decomposition increases from calcium to zinc.

(x) **Chlorides :** The chlorides are highly deliquescent solids, soluble in water, forming well-defined hydrates, e.g., $CaCl_2.6H_2O$; $MgCl_2.6H_2O$; $ZnCl_2.H_2O$. The $CaCl_2.6H_2O$ is only slightly hydrolysed on ignition, while the $MgCl_2.6H_2O$ and $ZnCl_2.H_2O$ are hydrolysed on ignition to MgO and ZnO respectively. The ease of hydrolysis of the salts increases from calcium salts (which are only *slightly* hydrolysed on ignition) to the zinc salts (which are *readily* hydrolysed).

(xi) **Sulphates :** All three metals form white crystalline sulphates e.g., $CaSO_4.2H_2O$; $MgSO_4.7H_2O$; $ZnSO_4.7H_2O$. Their solubility increases from calcium sulphate (which is *sparingly* soluble in water) to the zinc sulphate; both $MgSO_4$ and $ZnSO_4$ are freely soluble in water. $MgSO_4.7H_2O$ is isomorphous with $ZnSO_4.7H_2O$; they also form double salts of the type $K_2SO_4.MgSO_4.6H_2O$. But $CaSO_4$ does not form double sulphate like Mg and Zn.

(xii) **Nitrates :** All three metals yield deliquescent crystals, e.g., $Ca(NO_3)_2.4H_2O$: $Mg(NO_3)_2.6H_2O$; $Zn(NO_3)_2.6H_2O$. The nitrates are decomposed by heat to CaO, MgO and ZnO.

(xiii) **Sulphides :** The sulphides are white solids. CaS is sparingly soluble and is hydrolysed by water; MgS is soluble and hydrolysed. ZnS is insoluble in water and alkali but dissolves in all dilute mineral acids but not in acetic acid.

(xiv) **Cyanides :** $Ca(CN)_2$ and $Mg(CN)_2$ are soluble, but $Zn(CN)_2$ is insoluble in water but dissolves in KCN, yielding $K_2Zn(CN)_4$.

Cadmium

Most zinc ores contain small amounts of cadmium. A minor source is the rare mineral *greenockite*, CdS.

Extraction.—Cadmium is more volatile than zinc, and during the smelting of cadmiferous zinc ores the first portions of the *zinc dust* collecting in the receivers contain most of the cadmium as brown oxide CdO mixed with zinc oxide. The dust is mixed with coal and distilled in retorts at a low red-heat, when the crude metal containing 75 p.c. cadmium passes over. The product is distilled with charcoal in small clay or iron retorts, when fairly pure cadmium is obtained. $CdO + C = Cd + CO$.

Properties.—Cadmium is a tin-white, fairly soft, malleable and ductile metal. It burns in air, giving brown fumes of the oxide. It slowly dissolves in dilute hydrochloric and sulphuric acids, evolving hydrogen, and readily in dilute HNO_3 with evolution of oxides of nitrogen. Cadmium salts are usually colourless and are poisonous.

Uses.—Cadmium forms fusible alloys, e.g., *Wood's metal*, m.p. 71° ; is 1Cd, 1Sn, 2Pb, and 4Bi. Cadmium amalgam is used in Weston cell. Cadmium is added to silver to prevent staining. Cadmium (1 p.c.) is alloyed with copper for overhead tramway wires.

Compounds of Cadmium

Cadmium oxide, CdO, is formed on burning the metal in air, or igniting the carbonate or nitrate. It is a brown powder, and is basic in nature.

Cadmium hydroxide, $Cd(OH)_2$, is formed as a white precipitate by adding alkali hydroxide to a solution of a cadmium salt. It is soluble in ammonia but unlike zinc hydroxide it is insoluble in excess of alkali.

Cadmium carbonate, $CdCO_3$, is formed as a white precipitate by adding excess of ammonium carbonate to cadmium chloride solution, then ammonia till the precipitate just dissolves, and then heating on the water-bath.

Cadmium chloride, $CdCl_2.2\frac{1}{2}H_2O$, is efflorescent; it is rendered anhydrous by heating in a current of HCl gas. Like mercuric chloride, it is a poor electrolyte.

Cadmium Iodide, CdI_2, forms white leaflets; it is even a poorer electrolyte than the chloride, and is soluble in alcohol and acetone. During the electrolysis of its concentrated solution the cadmium tends to move to the anode rather than to the cathode. This is due to the formation of complex ions :

$$2CdI_2 \rightleftharpoons Cd[CdI_4] \rightleftharpoons Cd^{++} + CdI_4''$$

The complex $[CdI_4]''$ ion moves to the anode. On diluting the solution the complex begins to dissociate and cadmium moves to the cathode.

$$CdI_4'' \rightleftharpoons Cd^{++} + 4I'$$

Cadmium sulphate $3CdSO_4, 8H_2O$, is made by dissolving the oxide in sulphuric acid. It forms colourless monoclinic prisms, and is used in Weston cell.

Cadmium sulphide, CdS, is obtained as a bright yellow precipitate on passing H_2S into a *not too acid* solution of a cadmium salt (*cadmium sulphide is not precipitated from a strongly acid solution*). Cadmium sulphide is a costly yellow *pigment*; mixed with barium sulphate it forms **cadmiopone** (cf. lithopone).

Cadmium salts easily form complex cyanide, with potassium cyanide :

$$CdSO_4 + 4KCN = K_2[Cd(CN)_4] + K_2SO_4.$$

The complex cyanide partially dissociates, yielding Cd^{++} ions, and hence CdS is precipitated from cyanide solution by hydrogen sulphide—*a fact utilised for detecting cadmium in presence of copper* :

$$K_2[Cd(CN_4] \rightleftharpoons 2K^+ + [Cd(CN)_4]''; \quad [Cd(CN)_4]'' \rightleftharpoons Cd^{++} + 4CN'.$$

Mercury

Occurrence.— Mercury sometimes occurs native, but its chief source is the one **cinnabar,** mercuric sulphide, HgS, found at Almaden (Spain), Idria (Yugoslavia), Tuscany, and in smaller amounts in California, Texas, Mexico, Peru. China, Japan and India. The Almaden mine, worked since 415 B.C., is still the chief producer. The Spanish ore contains only 7 per cent mercury; the American ore less than 1 per cent.

Extraction.—Mercury is obtained by simply roasting cinnabar in air. The cinnabar is oxidised to mercuric oxide which decomposes at the temperature of the furnace, yielding mercury (b. p. 356·9°) which distils off:

$$2HgS + 3O_2 = 2HgO + 2SO_2; \quad 2HgO = 2Hg + O_2.$$

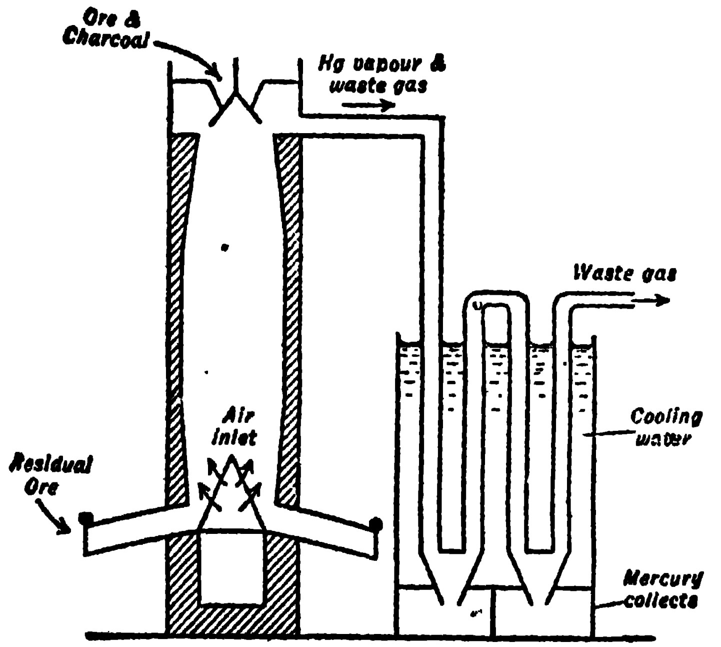


Fig. 174

Fig. 175

The ore is roasted with charcoal (fuel) in a shaft furnace (fig. 174). The mixture of ore and charcoal is fed to the top of a shaft furnace ;

the mixture passes down a series of sloping shelves in the shaft up which the hot gases from a fire-place are made to pass. The gases, leaving the furnace at the top, carry off the mercury in the form of vapour, and pass to a series of earthenware pipes having water-jackets for cooling, where the vapour of mercury is condensed to a liquid. The condensed liquid mercury is led into cisterns and bottled in iron flasks.

Rich ores may be distilled in retorts with lime or iron filings :

$$4HgS + 4CaO = 4Hg + 3CaS + CaSO_4 ; \quad HgS + Fe = FeS + Hg.$$

Purification of mercury.— Mercury is purified by distillation over chalk or iron, to decompose compounds of mercury, if any, and finally squeezing it through chamois leather. Commercial mercury usually contains traces of baser metals such as zinc or lead, which oxidise in air, forming an oxide scum on the surface; it then leaves a *tail* of grey residue when run over a glass surface. In the laboratory it is purified : (i) by filtering through chamois leather to remove the scum, (ii) by running it several times in a thin stream through a column of 5 p.c. nitric acid containing little mercurous nitrate in a glass tube (fig. 175), to dissolve out the baser metals, and (iii) finally distilling in vacuum.

Properties of mercury.—(i) Mercury, also known as **quick silver,** is a silver-white liquid, which does not tarnish in air when pure, and retains its lustre indefinitely.

It is the heaviest liquid known at room temperature, *with a very low vapour pressure* (less than 0·0002 mm. at 0°). *Its vapour is monatomic and extremely poisonous.*

(ii) Heated in air at about its boiling point for some days, mercury absorbs oxygen forming red mercuric oxide, which is again decomposed above 500°. $2Hg + O_2 \rightleftharpoons 2HgO$.

(iii) It is not attacked by water, steam, alkalis, or non-oxidising acids (HCl or dilute H_2SO_4). It dissolves in hot concentrated sulphuric acid, giving off sulphur dioxide (p. 303).

(iv) It dissolves in cold dilute nitric acid (p. 250).

In presence of sulphuric acid mercury reduces nitric acid quantitatively to nitric oxide. The reaction is used to estimate nitric acid by Lunge's nitrometer.

$$6Hg + 3H_2SO_4 + 2HNO_3 = 3Hg_2SO_4 + 4H_2O + 2NO.$$

(v) Mercury is directly attacked by the halogens, sulphur, nitrogen dioxide, and ozone. *It tails on exposure to ozone*, due to superficial oxidation to mercurous oxide.

(vi) It dissolves many metals, forming *amalgams,* but not the metals of the iron group, and hence it is commonly stored in iron bottles.

Uses of mercury.— It is used in the construction of physical apparatus such as barometer, thermometer and vacuum pumps; in the preparation of mercurial drugs, vermilion, and mercury fulminate for detonator; in the extraction of gold and silver; in the mercury vapour lamp for ultraviolet radiations; in making amalgams—sodium and aluminium amalgams are used as reducing agents; silver-amalgam is used in a dental filling; tin amalgam is used in coating mirrors.

Compounds of Mercury

Mercury forms two series of compounds, *the mercuric* compounds in which the metal is divalent, and the *mercurous* compounds containing the divalent group —Hg—Hg— in which the metal is apparently monovalent.

Mercurous oxide, HgO, is precipitated as a *dark-grey powder* by adding caustic soda to a solution of a mercurous salt:

$$Hg_2(NO_3)_2+2NaOH = Hg_2O+H_2O+2NaNO_3.$$

It decomposes at 100° or on exposure to light into mercuric oxide and mercury: $Hg_2O = HgO+Hg$.

Mercuric oxide, HgO, is prepared on a large scale as a red *crystalline powder* by heating to a moderate temperature a mixture of mercuric nitrate and mercury. $Hg(NO_3)_2+Hg = 2HgO+2NO_2$.

It is precipitated as a *yellow powder* by adding caustic soda to a solution of mercuric chloride: $HgCl_2+2NaOH = HgO+H_2O+2NaCl$.

It is a basic oxide, soluble in acids, but insoluble in water. It readily dissolves in potassium iodide solution giving an alkaline solution:

$$HgO+H_2O+4KI = 2KOH+K_2[HgI_4].$$

It dissociates into its elements on heating above 500°.

$$2HgO \rightleftharpoons 2Hg+O_2.$$

Mercurous carbonate, Hg_2CO_3, is precipitated as a yellow powder by adding potassium bicarbonate to mercurous nitrate solution. It decomposes at 130° or on exposure to light. $Hg_2CO_3 = HgO + Hg + CO_2$.

Mercuric carbonate, known only as a basic salt, is obtained as a brown precipitate of $HgCO_3$, 2HgO, by adding potassium carbonate to mercuric nitrate solution : $KHCO_3$ gives a brown precipitate of $HgCO_3$, 3HgO.

Mercurous chloride, calomel, Hg_2Cl_2, is prepared by heating an intimate mixture of: (i) mercuric chloride and mercury: $HgCl_2+Hg = Hg_2Cl_2$; (ii) mercuric sulphate, mercury and common salt, in an iron pot: $HgSO_4+2NaCl+Hg = Na_2SO_4+Hg_2Cl_2$.

Mercurous chloride sublimes on to the lid; the crust of the sublimate is collected, ground to powder, and *boiled with water to completely remove any adhering mercuric chloride.*

It is obtained as a white precipitate by adding dilute hydrochloric acid to mercurous nitrate solution.

$$Hg_2(NO_3)_2+2HCl = Hg_2Cl_2+2HNO_3.$$

It is a white amorphous powder, almost insoluble in water (about 0·4 mgm. per litre at 20°) and in dilute acids.

It dissolves in aqua regia, forming mercuric chloride, $Hg_2Cl_2+2Cl \rightleftharpoons 2HgCl_2$, and also to some extent in hot concentrated hydrochloric acid with the deposition of mercury.

$$Hg_2Cl_2+2HCl = Hg+H_2(HgCl)_4.$$

It blackens with ammonia—the black mass is a mixture of metallic mercury and infusible white precipitate of aminomercuric chloride:

$$Hg_2Cl_2+2NH_3 = Hg(NH_2)Cl+Hg+NH_4Cl.$$

Calomel vapour contains mercury and mercuric chloride due to thermal dissociation $Hg_2Cl_2 \rightleftharpoons Hg + HgCl_2$—perfectly dry calomel, however, sublimes unchanged on heating.

It is used in medicine as a purgative; and in making calomel electrode.

Mercuric chloride, corrosive sublimate, $HgCl_2$, is obtained by heating a dry mixture of equal weights of mercuric sulphate and common salt with a little manganese dioxide (being added as an oxidising agent to prevent the formation of mercurous chloride) in a long-necked flask on a sand bath. The mercuric chloride sublimes on to the cooler upper parts of the flask. The cake of the sublimate is removed, and the mercuric chloride is purified by recrystallisation from hot water: $HgSO_4+2NaCl = Na_2SO_4+HgCl_2$. It may also be obtained by heating mercury in chlorine: $Hg+Cl_2 = HgCl_2$.

It forms colourless needles, m. p. 227°, sparingly soluble in cold but freely in hot water. It also dissolves readily in alcohol and ether.

It reacts with boiling solution of ammonia, giving the *infusible white precipitate,* which is hydrolysed by digestion with water, yielding *chloride of Millon's base.*

$$HgCl_2+2NH_3 = Hg(NH_2)Cl+NH_4Cl$$

$$H_2N\text{-}Hg\text{-}Cl+H\text{-}O\text{-}H+H_2N\text{-}Hg\text{-}Cl = H_2N\text{-}Hg\text{-}O\text{-}Hg\text{-}Cl+NH_4Cl.$$

Mercuric chloride reacts with gaseous ammonia, yielding the *white fusible precipitate,* $HgCl_2$, $2NH_3$.

It is reduced by stannous chloride to mercurous chloride and finally to grey metallic mercury.

$2HgCl_2+SnCl_2 = Hg_2Cl_2+SnCl_4$: $Hg_2Cl_2+SnCl_2 = 2Hg+SnCl_4$.

It reacts with potassium iodide in an aqueous solution, giving a *yellow* precipitate (which rapidly turns *red*) of mercuric iodide, soluble in excess of potassium iodide solution, forming potassium mercuric iodide. $HgCl_2+2KI = 2KCl+HgI_2$; $HgI_2+2KI = K_2HgI_4$.

Nessler's reagent is a solution of potassium mercuric iodide made strongly alkaline with caustic potash. It produces a yellow solution of iodide of Millon's base, $H_2N\text{-}Hg\text{-}O\text{-}Hg\text{-}I$, with a trace of ammonia or ammonium salts; the reagent gives a brown precipitate with excess of ammonia.

Mercuric chloride is very poisonous, the fatal dose being 0·2—0·4 gm., the antidote is the raw white of an egg, which is coagulated, followed by emetic.

It is used as an antiseptic—1·1% solution is used in sterilising hands and surgical instruments; in preserving skins, as a bactricide.

Mercurous nitrate, $Hg_2(NO_3)_2$, is prepared in solution by the action of cold dilute nitric acid of sp. gr. 1·14 upon an excess of mercury; the solution deposits colourless crystals of the dihydrate, $Hg_2(NO_3)_2,2H_2O$. It is soluble in water containing nitric acid, but with pure water it forms an insoluble white basic nitrate. It decomposes on heating thus: $Hg_2(NO_3)_2 = 2HgO + 2NO_2$.

Mercuric nitrate, $Hg(NO_3)_2$, is prepared by dissolving mercury or mercuric oxide in hot concentrated nitric acid, or by heating mercurous nitrate with nitric acid; it separate from solutions in colourless deliquescent crystals of the monohydrate, $Hg(NO_3)_2$, H_2O.

It is decomposed by water, forming an insoluble white basic nitrate, which on heating, finally yields mercuric oxide. It is, therefore, dissolved in dilute nitric acid.

Mercurous sulphate, Hg_2SO_4, is prepared by heating excess of mercury with concentrated sulphuric acid, and deposited as white crystalline powder by diluting the acid solution with water, since it is sparingly soluble in water, but readily soluble in concentrated sulphuric acid. It is hydrolysed by water to a basic sulphate. It is used as a depolariser in the standard Weston cell.

Mercuric sulphate, $HgSO_4$, is prepared by boiling mercury with one and a half times its weight of concentrated sulphuric acid, it crystallises from the strong acid solution in silvery plates. $Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2$.

It is hydrolysed by water, forming an insoluble lemon-coloured basic sulphate.

Mercuric sulphide, HgS, occurs in nature as cinnabar. It is obtained by triturating mercury and sulphur with a little caustic potash solution. The black mass of mercuric sulphide produced is heated to about 50° with the addition of a little more alkali, when it slowly become red and crystalline. The product is washed with water and dried. $Hg + S = HgS$.

If H_2S is passed through a solution of a mercuric salt, at first a white, then yellow, brown, and finally a black precipitate of mercuric sulphide, HgS, is formed—the white precipitate of $HgCl_2, 2HgS$ is decomposed by H_2S.

$3HgCl_2 + 2H_2S = HgCl_2,2HgS + 4HCl$: $HgCl_2,2HgS + H_2S = 3HgS + 2HCl$
The black precipitate becomes red on sublimation.

It is insoluble in water, in yellow ammonium sulphide, in boiling hydrochloric or dilute nitric acid, but readily dissolves in aqua regia, and in potassium and sodium sulphide solutions.

It is used as the red pigment *vermillion*; in medicine as '*makaradhwaja*'.

Detection of Mercury.—All mercury compounds, on being heated with an excess of sodium carbonate or soda lime in a bulb-tube, deposit a shining mirror of metallic mercury. $2HgCl_2 + 2Na_2CO_3 = 2Hg + 4NaCl + 2CO_2 + O_2$.

If a piece of bright copper foil is immersed into a solution of a mercury salt, it becomes coated with a dull film of mercury which becomes bright and silvery on rubbing. $HgCl_2 + Cu = CuCl_2 + Hg$.

The mercurous and mercuric salts in solution are distinguished as follows :

Reagents	Mercurous salt	Mercuric salt
(i) Dilute HCl	White ppt. of Hg_2Cl_2	No precipitate
(ii) H_2S	Black ppt. $HgS + Hg$	White, then yellow, brown, and finally black ppt. of HgS
(iii) $SnCl_2$ solution	Grey ppt. of Hg	White to grey ppt.
(iv) KI solution	Green ppt. of Hg_2I_2	Scarlet ppt. of HgI_2
(v) NaOH solution	Black ppt. of Hg_2O	Yellow ppt. of HgO
(vi) NH_4OH	Black precipitate	White precipitate

Exercises

1. What are the chief sources of magnesium, and how is the metal extracted? Discuss its chemical relationship with calcium and zinc. Describe the preparation and uses of : anhydrous magnesium chloride, magnesium sulphate, magnesium oxide.

2. How does calcium occur in nature? Mention at least *three* compounds of calcium of commercial importance. Outline the preparation of : calcium, quick lime, calcium hydride, calcium carbide, plaster of Paris, and describe the action of water upon each of these substances. *Calcutta* '44.

3. Name the chief ores of zinc. How is the metal extracted and purified? What is the important by-product obtained during the metallurgical operation?

Describe the action of nitric acid, and caustic soda upon zinc. State the uses of the metal and its alloys. How is zinc detected?

4. How does mercury occur in nature, and how is it extracted from the native sulphide? Describe the preparation of pure mercury from a commercial specimen. Starting from metallic mercury, how would you prepare: mercurous nitrate, mercurous chloride, mercuric chloride? How would you distinguish between mercurous and mercuric compounds? *Punjab* '45.

5. Describe the preparation of chlorides of mercury. How can these salts be distinguished from one another and from silver chloride? How would you detect the presence of mercuric chloride in a specimen of mercurous chloride, and remove this impurity if present? Describe the action of caustic soda and ammonia on mercurous and mercuric salts.

6. Describe what happens when: (a) a mixture of magnesium oxide and coke is heated in chlorine, (b) the hexahydrate of magnesium chloride is heated, (c) precipitated magnesium hydroxide is shaken with ammonium chloride, (d) carbon dioxide is passed into a suspension of chalk in water, (e) calcium is heated in hydrogen, (f) caustic soda is gradually added to a solution of zinc sulphate, (g) zinc dust is added to a solution of silver nitrate, (h) calcium oxide is strongly heated in chlorine, (i) mercuric chloride is strongly heated with excess of soda lime, (j) mercuric sulphate is heated with mercury and common salt, (k) stannous chloride solution is added to mercuric chloride solution, (l) ammonia is added to calomel.

7. Give the preparation and uses of plaster of Paris, quick lime, anhydrous magnesium chloride, zinc white, white vitriol, lithopone, calomel, and corrosive sublimate. How would you show that calomel contains mercury?

8. Compare the physical and chemical properties of the elements Mg, Ca and Zn, illustrating your answer with reference to their oxides, hydroxides and carbonates. *Calcutta* '56.

9. How would you prepare (i) anhydrous magnesium chloride, (ii) magnesium sulphate, and (iii) magnesium carbonate, starting from native magnesite?

XXX

ALUMINIUM

Aluminium, along with boron, is placed in group III of the periodic table.

	At. no.	At. wt.	Density	At. vol.	M.p.	B.p.
Boron	5	10·82	2·34	4·62	2300°	2550°
Aluminium	13	26·97	2·70	10·00	659·8°	>2220°

Occurrence, etc.—Aluminium is not found native, but its compounds are widely distributed in nature. It occurs to the extent of 8% in earth's crust in many silicate rocks and clays. Important aluminium minerals are as:

(i) *silicates*: *felspar*, $K_2O.Al_2O_3$ $6SiO_2$, and *kaolin* (china clay), Al_2O_3, $2SiO_2$. $2H_2O$; also *micas*, *garnet* and *tourmaline*.

(ii) *oxides*: The oxide Al_2O_3 is found anhydrous as *corundum* and *emery* or hydrated as *diaspore*, Al_2O_3. H_2O; *bauxite*, Al_2O_3. $2H_2O$; *gibbsite*, Al_2O_3. $3H_2O$. The precious stones valued as gems, *e.g.*, *ruby* (red), *amethyst* (violet), *sapphire* (blue), *topaz* (yellow). and *emerald* (green), consist of aluminium oxide coloured by traces of oxides of Fe, Co, Cr, Mn and Ti.

(iii) *fluoride*: cryolite, AlF_3. 3NaF; it is found in Greenland only.

(iv) *phosphate*: *turquoise*, $AlPO_4$. $Al(OH)_3$. H_2O, coloured blue by the presence of copper phosphate.

Other minerals are *spinel*, MgO. Al_2O_3; *chrysoberyl*, BeO. Al_2O_3; *alunite*, $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$.

Clay is formed by the disintegration of *ortho clase or* (*potash*) *felspar* which is a constituent of granite rocks, due to the weathering action of water and carbon dioxide.

$$K_2O.\ Al_2O_3.\ 6SiO_2 + 2H_2O + CO_2 = K_2CO_3 + Al_2O_3.\ 2SiO_2.\ 2H_2O + 4SiO_2.$$

Pure clay or kaolin (china clay) is white and consists of hydrated aluminium silicate, $Al_2O_3.\ 2SiO_2.\ 2H_2O$, but most clays are coloured due to presence of ferric oxide and other impurities.

Aluminium is manufactured from bauxite, $Al_2O_3, 2H_2O$. Important deposits of bauxite are found in the south of France, South America, Ireland and U.S.A. Bauxite occurs in India in Katni, Belgaum, Kohlapur, Ranchi, Bombay, Madras, and Bhopal, etc. Aluminium is extracted from bauxite by Aluminium Corporation of India, near Asansol in Bengal, and by Indian Aluminium Company at Alwaye in Travancore. No cheap method is available to extract the metal from clay. Analysis of few samples of bauxite :

Source	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	H_2O
Katni	1·2	8·8	60·2	2·6	25·4
Ranchi	0·3	7·4	66·9	5·9	21·4

Extraction.— Aluminium was first isolated is 1827 by Wohler by the action of potassium upon aluminium chloride. Aluminium was formerly obtained by converting alumina into chloride by heating with charcoal in chlorine, and then reducing sodium aluminium chloride with sodium :

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO\ ;\quad NaAlCl_4 + 3Na = 4NaCl + Al.$$

The metal is now exclusively obtained from *bauxite* by an electrolytic process simultaneously discovered in 1886 by Hall in America and Heroult in France.

Crude bauxite contains the impurities *iron oxide and silica* which must be removed before electrolysis, otherwise the resulting aluminium contains iron and silicon, and is readily corroded by water. Hence the manufacture of aluminium consists of two steps: (a) *purification of the bauxite, and* (b) *electrolysis of purified bauxite.*

(a) Purification of the bauxite: Bayer's process.—The calcined bauxite is finely ground, and then digested with a strong (sp. gr. 1·45) solution of caustic soda in an autoclave under 80 lbs. pressure at 150° for 2 to 8 hours when aluminium oxide goes into solution as sodium aluminate, the iron oxide remaining undissolved. When the digestion is complete, the hot sodium aluminate solution is filtered from the insoluble oxide of iron and other impurities (*red mud*). The solution is then diluted, slowly cooled and agitated for several hours with freshly precipitated hydrated alumina, when the sodium aluminate undergoes hydrolysis and hydrated alumina (β-alumina) is precipitated. The precipitate is filtered, washed and calcined to pure alumina (99·55 per cent) in a rotary kiln at 1100°C.

$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O\ ;$$

$$2NaAlO_2 + 4H_2O \rightleftharpoons 2Al(OH)_3 + 2NaOH\ ;\quad 2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

The filtrate contains caustic soda; it is concentrated by evaporation and used again for digestion of a fresh charge.

Bauxite with high silica content cannot be treated by Bayer's process, since much aluminium is lost due to the formation of insoluble sodium aluminium silicate. Bayer's process is best adapted to bauxite containing 55 to 60% Al_2O_3, and relatively low in silica (below 7% SiO_2) content.

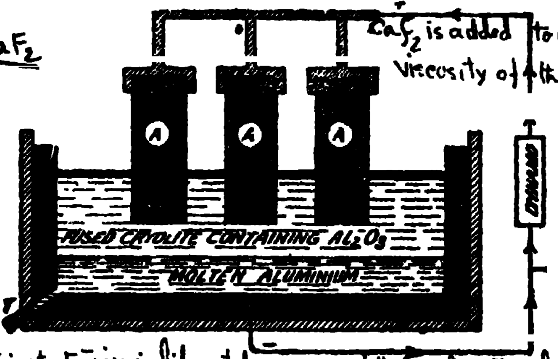
In the old process the bauxite is heated to bright redness with sodium carbonate, and the mass is readily lixiviated with water—the resulting sodium aluminate and sodium silicate dissolve, ferric oxide remaining insoluble. Aluminium hydroxide is precipitated from the solution by carbon dioxide at 50° to 60°, and is ignited to the oxide. $Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CO_2$;

$$2NaAlO_2 + 3H_2O + CO_2 = Na_2CO_3 + 2Al(OH)_3$$

Bauxite may also be purified by heating with coke at 1800° in a current of nitrogen (obsolete **Serpek's process**)—the resulting aluminium nitride being decomposed by hot water, yielding ammonia and aluminium hydroxide which is ignited to the alumina.

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO;\quad AlN + 3HOH = NH_3 + Al(OH)_3$$

(b) **Electrolysis of alumina.**—Aluminium is obtained by the electrolysis of the pure alumina (20 parts) dissolved in a bath of fused cryolite (60 parts) and fluorspar (20 parts)—the CaF_2 melt at 950°C, the passage of current supplying sufficient heat to maintain the required temperature. The electrolysis is carried out in an iron tank (fig. 176) lined with blocks of carbon which forms the cathode—the anode is a set of hard carbon (low-ash petroleum coke) rods A suspended in the tank from copper clamps. During electrolysis aluminium (m.p. 659°) is liberated at the cathode and collects in the liquid state on the floor of the cell whence it is tapped out; oxygen is evolved at the anode which is burnt away to carbon monoxide—hence the charge is covered with a layer of coke to minimise the oxidation of the expensive anodes.



CaF_2 is added to decrease the viscosity of the sol.

Fig. 176

At first, F^- ion is liberated at the anode. F_2, being more electro-ve, replaces O_2 from Al_2O_3 and forms again AlF_3.

$$Al_2O_3 \rightleftharpoons 2Al^{+++} + 3O''$$

$$2Al^{+++} + 6e = 2Al \text{ (at cathode)};\quad 3O'' = 3O \text{ (at anode)} + 6e$$

Fresh alumina is added at intervals to supply that decomposed. When the supply of alumina in the bath gets exhausted the voltage suddenly jumps from 5 to 6 volts up to 40 or 60 volts (this is known as the *anode effect*), there being an increase in the resistance of the bath. When the anode effect occurs an electric lamp connected across the terminals of the cells which normally glows dimly, becomes very bright. This acts as a signal for the supply of fresh alumina into the bath. The voltage used is 5—6 volts and the energy consumption is 10 K.W.H. per lb.

Cryolite acts as a flux in the process—its only source is Greenland. Synthetic cryolite, free from silica, is made for use in the aluminium extraction by the reaction.

$$AlF_3 + 3NH_4F + 3NaNO_3 = AlF_3{,}3NaF + 3NH_4NO_3$$

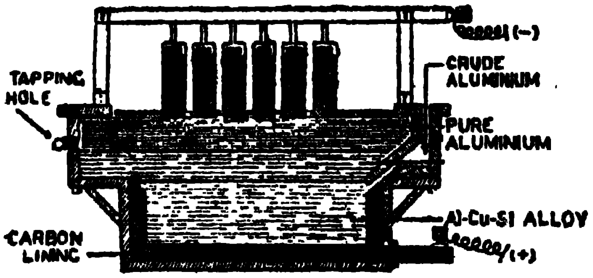


Fig. 177

(c) **Refining.**—The aluminium produced has a purity of 99%, its chief impurities being iron and silicon. The metal is refined electrolytically by **Hoope's process.** The electrolytic cell contains three liquid layers of different densities, Pure molten aluminium cathode at the top, liquid crude aluminium-copper alloy anode at the bottom, with a layer of molten mixture of

$AlF_3, 3NaF \rightleftharpoons Al^{+++} + 3Na^+ + 6F^-$ Cathode:— $Al^{+++} + 3e = Al$

Anode:— $3F^- - 3e = 3F$, $3F + 3F = 3F_2$

$\underline{2Al_2O_3 + 6F_2 = 4AlF_3 + 3O_2}$

cryolite, aluminium fluoride, barium fluoride and alumina electrolyte in between (fig. 177). In course of electrolysis aluminium dissolves out from the anode, and is deposited at the cathode—the refined Al has a purity of 99·99%.

Properties of aluminium.—(i) Aluminium is an extremely light (density 2·70), silver white metal, sufficiently malleable and ductile to be rolled into foil or drawn into wire. It has a high tensile strength and a good thermal and electrical conductivity.

(ii) It is coated with a protective film of aluminium oxide when exposed to air, and hence does not readily tarnish in air.

But corrosion occurs if the film is broken by amalgamation with mercury (by rubbing the surface with mercury or mercuric chloride).

Aluminium foil or powder burns in air with a bright flame when strongly heated, forming the oxide as well as the nitride.

$$4Al+3O_2=2Al_2O_3\,;\quad 2Al+N_2=2AlN.$$

(iii) Aluminium is not attacked by pure water owing to the protective oxide film on the surface; sea water or saline solutions readily attack it. Amalgamated aluminium decomposes water even in the cold. $2Al+6HOH=2Al(OH)_3+3H_2$.

(iv) It readily dissolves in hydrochloric acid. But it is scarcely attacked at all either by dilute sulphuric acid or by dilute or concentrated nitric acid. Hot concentrated sulphuric acid dissolves aluminium, yielding sulphur dioxide.

$$2Al+6HCl=2AlCl_3+3H_2\,;\quad 2Al+6H_2SO_4=Al_2(SO_4)_3+3SO_2+6H_2O.$$

Aluminium is corroded by organic acids, most rapidly when the acid is diluted or anhydrous.

(v) It readily dissolves in hot caustic soda or potash solution, forming aluminate: $2Al+2NaOH+2H_2O=2NaAlO_2+3H_2$.

(vi) It combines directly, when heated with nitrogen, chlorine, sulphur, and carbon, forming the nitride AlN, chloride, $AlCl_3$, sulphide, Al_2S_3, and carbide, Al_4C_3, respectively.

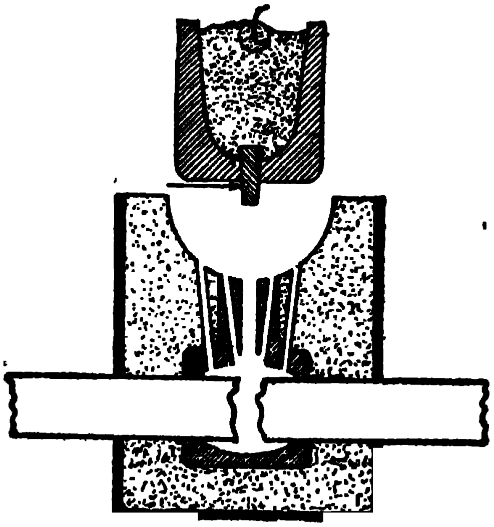


Fig. 178

(vii) Aluminium has a strong affinity for oxygen at and above 1000°, and the great evolution of heat resulting from its combination with oxygen is utilised in **Goldschmidt's thermit** or **aluminothermic** process for reducing metallic oxides (e.g., MnO_2 and Cr_2O_3) and for the preparation of molten metals *in situ*, *e.g.*, molten iron for welding rails and machine parts. *Thermite* is a mixture of aluminium powder and iron oxide. A mixture of aluminium filings (1 part) and iron oxide (3 parts) is ignited in a crucible by a fuse of magnesium, when a violent reaction occurs, producing molten iron at a temperature of about 2500°. The liquid iron is tapped from below directly on to the joint to be welded (fig. 178).

$$Fe_2O_3+2Al=2Fe+Al_2O_3+199{,}000 \text{ calories.}$$

Uses of aluminium.—(i) On account of its *lightness* and fair *tensile strength*, aluminium is used in making body of air-ships and motor cars; for the same reasons it is used for making alloys.

Alloy	Composition	Uses
(i) Magnalium	Al 98 Mg 2	Cheap balance, machined articles—the alloy can be worked on lathe.
(ii) Duralumin Y—alloy	Al 95 Cu 4 Mg 0·5 Mn 0·5 Al 92·5 Cu 4 Mg 1·5 Ni 2	Construction for aircrafts —the alloys are light, tough and resist corrosion.
(iii) Aluminium bronze	Al 10 Cu 90	Coins, utensils, photo-frames.
(iv) Alclad	Duralumin covered with a thin coating of Al	For making sea planes—the alloy resist corrosion by sea water.
(iv) Alnico	Steel 50 Al 20 Ni 20 Co 10	For making permanent magnets.

(i) On account of its good electrical conductivity (60% of that of an equal volume of copper, or 200% of that of a copper conductor of equal weight) it finds use in transmission wires. (iii) On account of its good thermal conductivity, it is used in making *cooking utensils*. (iv) Since it resists corrosion, it is used as *aluminium paint*—*aluminium* powder, produced by stamping thin aluminium sheet in oil, is used as the paint. Aluminium foils are used in wrapping cigarettes, etc. (v) Due to its great affinity for oxygen, aluminium is used in *thermite*—utilised in welding rails and machine parts, in incendiary bombs, and in the preparation of chromium and manganese and also as a reducing agent. Ammonal, a mixture of ammonium nitrate and aluminium powder, is used in explosive bombs. Aluminium powder finds use in fire-works.

Calorising is a process for the surface impregnation of iron, steel, copper, nickel, brass etc., with aluminium and is effected by heating the subject metal to about 1000°C with a mixture of finely divided aluminium and aluminium oxide in a reducing atmosphere of hydrogen—a thin outer coating of aluminium oxide forms the protective surface. Calorised non-ferrous metals and alloys, such as copper, nickel and brass, are resistent to oxidation at high temperatures or to acid liquors.

Steel is being now largely displaced by the light aluminium alloys which find modern uses in aircraft, machinery, and metal articles of all kinds.

Compounds of Aluminium

Aluminium oxide, alumina, Al_2O_3, occurs naturally as (i) colourless crystals in *corundum*—*emery* is an impure opaque variety; nealy hard as diamond they are used in polishing and grinding; and (ii) as coloured stones (p. 433).

Artificial gems are produced by dropping powdered alumina mixed with a little of other metallic oxides to obtain the desired colour (e.g. 2·5% chromic oxide for *artificial ruby*) through the centre of an oxyhydrogen flame and catching the fused mass on a rod of alumina.

Sapphire is similarly made from alumina with addition of a little magnetic iron oxide and titanium dioxide.

The mineral *bauxite* is valuable as a source of alumina and aluminium.

Pure alumina may be made by igniting aluminium hydroxide, aluminium sulphate or ammonium alum. An extremely infusible white powder, usually soluble in acids it becomes insoluble in acids after ignition above 850°. Ignited alumina is brought into solution as aluminate by fusion with an alkali. Alumina is an amphoteric oxide. Aluminium oxide is not reduced by hydrogen or carbon.

$$Al_2O_3 + 2NaOH \rightleftharpoons 2NaAlO_2 + H_2O.$$

Artificial corundum, known as **alundum,** is used as a basic refractory and abrasive. It is made by fusing bauxite with coke (3 percent) and iron 2 per cent) in an arc furnace at 3000°, when the impurities are reduced and settle at the bottom as ferro-silicon alloy—the upper layer being fused alumina which is cooled and crushed.

Aluminium hydroxide, $Al(OH)_3$, is thrown down as a white gelatinous mass from a hot solution of aluminium salts by ammonia even in presence of ammonium chloride:

$$Al_2(SO_4)_3 + 6NH_4OH = 2Al(OH)_3 + 3(NH_4)_2SO_4.$$

An amphoteric hydroxide, it readily dissolves in acids to form salts, and also in alkalis, caustic soda or potash, forming aluminates which are, however, largely hydrolysed.

$$Al(OH)_3 + NaOH \rightleftharpoons NaAlO_2 + 2H_2O.$$

Precipitated aluminium hydroxide readily carries down by adsorption colloidal substances and colouring matters, and hence the use of alum and aluminium salts : (i) in the clarification of water and sewage liquids; (ii) in waterproofing of fabrics; and (iii) in dyeing as mordants.

Partly dehydrated (at 200°—250°) aluminium hydroxide, called *alumina gel,* is used as a drying agent and as an adsorbent (e.g. in *chromatographic analysis*).

Aluminium hydroxide is precipitated from its salt solutions by sodium carbonate:

$$Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 2Al(OH)_3 + 3Na_2SO_4 + 3CO_2.$$

As alumina is a very weak base, no aluminium carbonate is known.

Aluminium chloride, $AlCl_3$, is prepared by dissolving the metal or hydroxide in hydrochloric acid and may be crystallised out from the solution as the hexa hydrate $AlCl_3,6H_2O$. The hydrate is hydrolysed to alumina on heating: $2(AlCl_3, 6H_2O) = Al_2O_3 + 6HCl + 9H_2O$. *Anhydrous aluminium chloride* is obtained: (i) by strongly heating to 1600°C a mixture of alumina and coke in a current of chlorine—the aluminium chloride being volatalised and condensed.

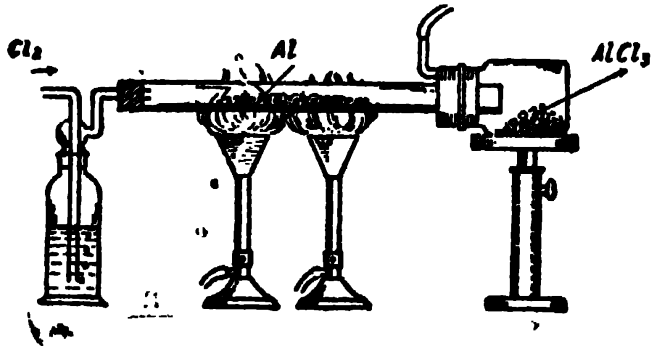


Fig. 179

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$

(ii) by passing dry chlorine or hydrogen chloride (dried by concentrated sulphuric acid) over heated aluminium turnings in a hard glass tube (fig. 179); anhydrous aluminium chloride sublimes and collects in a bottle, which is tightly corked at the end of the experiment to exclude moisture.

$$2Al+3Cl_2=2AlCl_3\,;\quad 2Al+6HCl=2AlCl_3+3H_2.$$

Anhydrous aluminium chloride is a white, crystalline, extremely deliquescent substance which fumes in moist air and sublimes without fusion at 183°. It is soluble in water, the solution is acid due to hydrolysis: $AlCl_3+3HOH \rightleftharpoons Al(OH)_3+3HCl$.

Its vapour density up to 400° corresponds to the formula Al_2C_6; dissociation to $AlCl_3$ begins above 400° and is complete at 900°.

Aluminium nitrate, $Al(NO_3)_3$, $9H_2O$, is obtained by mixing solutions of aluminium sulphate and lead nitrate, filtering, and concentrating the filtrate to crystallisation.

Aluminium sulphate, $Al_2(SO_4)_3$, is made by dissolving alumina in hot concentrated sulphuric acid; ill-defined crystals of aluminium sulphate, $Al_2(SO_4)_3$, $18H_2O$, are deposited on cooling the solution. They are recrystallised from water containing alcohol.

$$Al_2O_3+3H_2SO_4=Al_2(SO_4)_3+3H_2O.$$

Crude aluminium sulphate containing ferric sulphate (which cannot be separated by crystallisation) is made by digesting bauxite with 62% sulphuric acid—the solution is evaporated to a solid, called **alumino-ferric,** largely used in purifying water and sewage.

Aluminium sulphate may however, be crystallised after reducing the ferric sulphate to the ferrous state by sodium sulphide.

Crude aluminium sulphate is also made by digesting china clay (**kaolin**) with concentrated sulphuric acid.

$$Al_2O_3,\ 2SiO_2,\ 2H_2O\ (\text{kaolin})+3H_2SO_4=Al_2(SO_4)_3+2SiO_2+5H_2O.$$

A colourless, crystalline solid, it is soluble in water—the solution is acid due to hydrolysis. $Al_2(SO_4)_3+6H_2O \rightleftharpoons 2Al(OH)_3+3H_2SO_4$. It forms an important series of double salts, known as alums. The hydrate forms the anhydrous salt on gentle heating, but at a red heat it decomposes into alumina, sulphur dioxide, and oxygen.

$$2Al_2(SO_4)_3=2Al_2O_3+6SO_2+3O_2.$$

It is used as a mordant in dyeing and calico-printing; in the sizing of paper; in purifying sewage and water; in 'foam' fire extinguishers; in tanning kid leather.

Alums.—The name alum was given originally to the double-salt, potassium aluminium sulphate, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$. But the name *alum* is now given to all double salts of the type M_2SO_4, $R_2(SO_4)_3$, $24H_2O$, where M is a monovalent metal and R a trivalent metal. M may be Na, K, Rb, Cs or NH_4; R may be Fe, Al, Cr, Mn, or Co. The alums are isomorphous and form octahedral crystals. Examples are:

Potash or common alum ...	K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$.
Ferric ammonium alum ..	$(NH_4)_2SO_4$, $Fe_2(SO_4)_3$, $24H_2O$.
Chrome alum	K_2SO_4, $Cr_2(SO_4)_3$, $24H_2O$.
Ammonia alum	$(NH_4)_2SO_4$, $Al_2(SO_4)_3$, $24H_2O$.

Potash alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$, deposits in colourless octahedral crystals when a hot solution containing equimolecular quantities of potassium and aluminium sulphates is set aside to crystallise.

Alum is made commercially from: (i) **Bauxite**—Bauxite is ground to powder and then digested at steam heat with 62 per cent sulphuric acid in a lead-lined steel tank fitted with steam coils and then treated with barium sulphide to reduce the ferric sulphate to the ferrous state —the clear aluminium sulphate solution is either decanted or filtered, after settling, and then mixed with the correct amount of potassium sulphate. The mixed solution on concentration and cooling yields alum crystals. It may be purified by recrystallisation and obtained completely free from iron. $Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O$.

(ii) **Alunite** or **alum stone,** $K_2SO_4,Al_2(SO_4)_3,4Al(OH)_3$—the alunite is calcined and then digested with sulphuric acid to convert the alumina to aluminium sulphate. Required amount of potassium sulphate is then added to the solution and the alum is allowed to crystallise.

Formerly alum was obtained by simply calcining alunite in air, leaching with water, and crystallising—as so made it is called **Roman alum.**

(iii) **Alum shale** which is aluminium silicate containing iron pyrites, FeS_2. The shale is roasted in heaps, when the oxidation of the pyrites gives ferrous sulphate and sulphuric acid, which converts aluminium silicate to aluminium sulphate. The roasted mass is extracted with water; requisite quantity of potassium chloride is added to the extract and the solution is crystallised for alum.

Potash alum forms colourless octahedral crystals having an astringent taste. It dissolves in water, and melts at 92°. It loses all its water of crystallisation at 200°, leaving a residue of anhydrous sulphate, known as *burnt alum.*

Alum is used as 'styptic' to stop bleeding from small cuts. Alum is put to the same uses as aluminium sulphate (*vide supra*).

Ammonium alum, $(NH_4)_2SO_4,Al_2(SO_4)_3,24H_2O$, deposits from solution as colourless octahedral crystals, m.p. 95°. It leaves a residue of pure alumina on ignition.

$$(NH_4)_2SO_4,\ Al_2(SO_4)_3,\ 24H_2O = 2NH_3 + 4H_2SO_4 + Al_2O_3 + 21H_2O.$$

Ultramarine.—The deep blue mineral lapis lazuli is sodium aluminium silicate containing sulphur—the artificial form is ultramarine. Kaolin, soda ash or sodium sulphate, sulphur, wood charcoal or resin are taken in a closed crucible and heated to redness in absence of air when white ultramarine results—blue ultramarine of commerce is obtained by heating the white product with powdered sulphur in air. It is not attacked by soap or soda and hence its use in laundering. It is largely used in white washing walls and in sugar refinery. It is decomposed by acids with evolution of hydrogen sulphide.

Aluminium sulphide, Al_2S_3, is made by direct union of its elements. It is completely hydrolysed by water: $Al_2S_3 + 6HOH = 2Al(OH)_3 + 3H_2S$.

Hence only aluminium hydroxide is precipitated on adding ammonium suphide to a solution of aluminium salt.

$$Al_2(SO_4)_3 + 3NH_4HS + 6H_2O = 3NH_4HSO_4 + 2Al(OH)_3 + 3H_2S.$$

Detection of aluminium.— (i) Aluminium compounds, mixed with sodium carbonate and heated on charcoal in a blow pipe flame, yields a *white incandescent mass*, which on being moistened with cobalt nitrate and heated again, turns *blue* **(Thenard's blue).** (ii) Ammonium hydroxide, when added to a solution of an aluminium salt, gives a white gelatinous precipitate of aluminium hydroxide, even in presence of ammonium chloride; the precipitate dissolves in caustic soda or potash forming aluminate, and is reprecipitated by heating with ammonium chloride:

$$NaAlO_2 + NH_4Cl + H_2O = Al(OH)_3 + NH_3 + NaCl.$$

Tin and Lead

Tin and lead belong to group IVB in the periodic classification. Tin closely resembles lead—both are heavy, lustrous metals of low melting point, but they differ in that the most stannic compounds are more stable than stannous compounds. While the reverse is usually true for lead compounds. Thus stannous chloride is a reducing agent and is readily oxidised in air; the plumbous chloride is not a reducing agent and may be made from plumbic chloride by heat; $PbCl_4 = PbCl_2 + Cl_2$. Also the plumbous oxide, PbO, is more basic than stannous oxide, SnO. The table shows the properties of tin and lead.

	Tin	Lead
Physical properties	At. no. 50; Density 7·5; M.p. 232°C. At. wt. 118·7; At. vol. 16·3; B.p. 2260°C. Malleable and conductor of electricity; exhibits allotropy; valency 2 and 4.	At. no. 82; Density 11·34; M.p. 327·4°C. At. wt. 207·21; At. vol. 18·27; B.p. 1620°C. Malleable and conductor of electricity; *marks paper;* valency 2 and 4.
Chemical properties	Untarnished in air; burns to SnO_2: Slowly soluble in dilute HCl; easily soluble in conc. HCl and dilute HNO_3. Conc. HNO_3 gives metastannic acid.	Tarnishes in air; burns to PbO mainly. Insoluble in dilute HCl; slowly soluble in hot conc. HCl, but readily in dilute HNO_3; scarcely attacked by conc. HNO_3.
Oxides	SnO amphoteric. SnO_2 amphoteric, not an oxidising agent.	PbO amphoteric; more basic than SnO. PbO_2 amphoteric, oxidising agent. Other oxides are Pb_2O_3 and Pb_3O_4.
Hydride	SnH_4 (stannane), gaseous.	PbH_4 (plumbane), gaseous.
Chloride	$SnCl_2$, a white salt, readily hydrolysed by water; a reducing agent, readily oxidises in air.	$PbCl_2$, a white salt, sparingly soluble in cold but more soluble in hot water, in which it is not hydrolysed. Not a reducing agent.
	$SnCl_4$, a fuming colourless liquid, readily hydrolysed by water.	$PbCl_4$, yellow fuming liquid: unstable, readily hydrolysed by water.
Sulphide	SnS brown; SnS_2 yellow—both precipitate in acid solution: soluble in yellow ammonium sulphide.	PbS black, precipitates in acid solution: insoluble in yellow ammonium sulphide.

Tin

Occurrence.—Tin occassionally occurs *native*, but its principal ore is **cassiterite or tin stone,** SnO_2, found in the Malay Peninsula which alone accounts for about a third of the world production, Bolivia, Indonesia, Cornwall, Burma and elsewhere. Tin stone occurs in Bihar and Orissa, especially in the Hazaribagh district. The ancient Indians, Chinese, Egyptians and Babylonians were acquainted with the use of bronze, an alloy of copper and tin.

Extraction.—The ore contains only 1 to 5 per cent tin stone; the rest are chiefly *silica* and *wolframite* (iron tungstate, $FeWO_4$), iron pyrites, and arsenical pyrites, and sometimes copper pyrites. The ore is concentrated, and then smelted to give crude tin which is finally refined.

Concentration.—(i) Washing.— The ore is crushed and washed in a current of water which carries away the light silicious gangue (sp.gr. 2·5), leaving the heavy tin stone (sp. gr. 6·4—7·1) and wolframite (sp. gr. 7·1—7·9) etc., behind. The wolframite being as heavy as tinstone cannot be separated by washing; it is removed by roasting and electromagnetic separation.

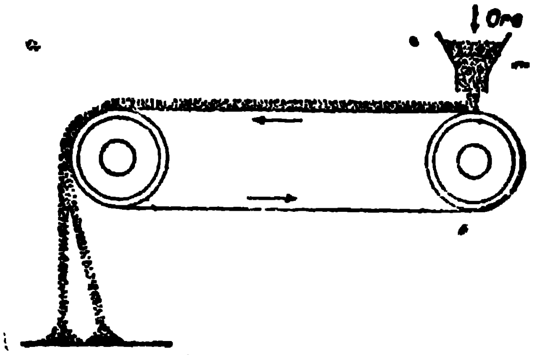


Fig. 180

(ii) **Roasting.**—The impure tin stone is then roasted in a current of hot air in an inclined revolving tube-furnace, when arsenic and sulphur are expelled as volatile oxide; most of the iron is converted to the magnetic oxide, Fe_3O_4, and copper forms oxide and sulphate.

(iii) **Magnetic separation.**—The roasted ore is then *treated in a magnetic separator*—the powdered ore being carried by a travelling belt over an electro-magnetic roller; tin stone, being non-magnetic, falls off undeflected whereas the magnetic wolframite and iron oxide are attracted by a magnet and collect in a separate heap (fig. 180).

The wolframite may also be removed by heating the roasted ore with soda ash at 600°, when soluble sodium tungstate is formed.

(iv) **Washing.**—The mass is finally washed with water to dissolve copper sulphate and to remove ferric oxide and other light materials. The tin-concentrate contains about 65 to 90 per cent tin stone and is known as *black tin.*

Smelting.—The black tin is mixed with one-fifth of its weight of crushed *anthracite* and some *lime* and fluorspar to act as a flux, and smelted at 1200°—1300° in a reverberatory furnace when the tin oxide is reduced to the metal. The molten tin and slag form two layers, and are run out separately: $SnO_2 + 2C = Sn + 2CO$.

The slag contains much tin, about 5%, and is worked up by smelting with carbon. The liquid tin is cast into ingots, and sent to the refinery.

Refining.—The crude tin is refined by *liquation*, i.e., by heating the ingots on the sloping hearth of a reverberatory furnace, when the easily fusible tin (m.p. 232°) melts and runs away leaving behind a dross of an alloy of tin with iron, copper, tungsten, and arsenic. The liquated tin is further treated by *poling*, *i.e.*, the liquid tin is stirred with pieces of green wood so that a large surface is exposed to the air, when the remaining impurities are oxidised, and separate as scum on the surface, and are skimmed off. The tin so obtained is of over 99 per cent purity. The scum and dross contain much tin, and are worked up by smelting. Tin may be refined electrolytically—the impure metal is the anode and pure tin the cathode, and the electrolyte is an acidic solution of stannous sulphate. During electrolysis tin dissolves from the anode and is deposited on the cathode.

Properties of tin—(i) Tin is a soft and easily fusible (m. p. 232°), white lustrous metal, which is notably crystalline.

A rod of tin, when bent, emits a creaking sound **(cry of tin)** due to the rubbing of the crystals against each other. The metal is very malleable to be rolled into *foil*, but not very ductile to be drawn.

(ii) It exists in two main allotropic forms, *white tin* (sp. gr. 7·28) and *grey tin* (sp. gr. 5·62), transition temperature being 13·2 ;

$$\text{grey tin} \rightleftharpoons \text{white tin}$$

Below 13·2° the ordinary white tin passes into grey tin, the transformation being accompanied by expansion and disintegration of the metal. The transformation is the quickest at —50°. Tin articles, therefore, crumble to powder during severe winters and are said to be attacked by **tin plague.**

(iii) It is neither tarnished nor corroded in air at room temperature, but when heated in air it is converted to white stannic oxide, SnO_2.

(iv) It is not attacked by water but is readily attacked by mineral acids. At very high temperatures tin slowly decomposes steam: $2H_2O+Sn=SnO_2+2H_2$. It slowly dissolves in dilute hydrochloric or sulphuric acids, giving stannous salt and hydrogen—the action of hot concentrated HCl is fairly rapid. Hot concentrated H_2SO_4 reacts with tin, giving off sulphur dioxide. Nitric acids also acts on tin (p. 250).

$$Sn+2HCl=SnCl_2+H_2\ ;\quad Sn+2H_2SO_4=SnSO_4+2H_2O+SO_2.$$

(v) It dissolves in hot caustic soda or potash, giving stannite and hydrogen: $Sn+2NaOH=Na_2SnO_2+H_2$; the stannite is readily oxidised to stannate in presence of air.

(vi) It combines directly, when heated, with chlorine and sulphur, to form respectively stannic chloride $SnCl_4$, and stannous sulphide, SnS.

$$Sn+2Cl_2=SnCl_4\ ;\quad Sn+S=SnS.$$

Uses of tin.— (i) Tin is resistant to atmospheric corrosion, and hence its applications as *tin foils* for packing perishable materials, and for *tinning* or *tin-plating* iron, copper and lead.

Tin plate is made by dipping sheets of mild steel (previously cleaned by pickling with dilute H_2SO_4 to remove the oxide-scale) into molten tin (covered with a layer of fused zinc chloride to prevent formation of scum of tin oxide); the sheets then pass into a bath of molten palm oil, and finally through a pair of rollers to squeeze the excess of tin. The tin forms a thin continuous layer on the surface of iron. The tin plate vessels are used in the storage of petrol, kerosene, confectionary, and tobacco. Tin cans are used for canning meat and fruit.

Brass and copper utensils are tinned to prevent the poisoning of food; *tinning* is effected by brushing molten tin (containing rosin and sal ammoniac as fluxes) over the surface.

Tinning is less serviceable than galvanisation, when once the surface of iron is exposed, since iron alone is attacked as it stands above tin in the electrochemical series—a galvanic cell is set up, and hence iron dissolves more rapidly than when no tin is present. Zinc is, however, more electro-positive than iron, and is therefore preferentially dissolved under similar conditions.

Large quantities of tin are recovered from scrap tin plate by exposing it to chlorine gas, which converts the tin to the volatile stannic chloride.

(ii) Tin is a constituent of many useful alloys : *pewter* (Sn 80; Pb 20), *solder* (Sn 50; Pb 50), *babbit metal* (Sn 90; Sb 7; Cu 3), and *Britania metal* (Sn 90; Sb 10). *Bronze, bell metal,* and *gun metal* are alloys of tin and copper in different proportions. *Tin amalgam* is used in coating glass mirrors.

Compounds of Tin

Tin forms two series of compounds: *stannous* compound where the metal is bivalent, and *stannic compounds* in which tin is quadrivalent. **Stannous** compounds *are reducing agents*, since they readily pass by oxidation to the stannic state. Stannous chloride, for example quantitatively reduces a hot solution of ferric chloride. $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$.

Stannous oxide. SnO, a dark-grey powder, is prepared by heating, in the absence of air, the white precipitate of stannous hydroxide, formed by the action of caustic soda upon stannous chloride solution.

$$SnCl+2NaOH = 2NaCl+Sn(OH)_2;\ Sn(OH)_2 = SnO+H_2O.$$

It is also obtained by heating stannous oxalate in the absence of air:

$$SnC_2O_4 = SnO + CO + CO_2.$$

It is readily oxidised to stannic oxide, SnO_2, on exposure to air. *An amphoteric oxide,* it dissolves in acid, forming stannous salts, and in dilute alkalis in the absence of air, yielding stannites: $SnO+2NaOH=Na_2SnO_2+H_2O$. *The stannite solution has strong reducing properties.* Stannous hydroxide also dissolves in alkali to give a stannite. $Sn(OH)_2+2NaOH=Na_2SnO_2+2H_2O$.

Stannic oxide, SnO_2, a white powder, is prepared by burning tin at a white heat in air or by igniting metastannic acid, formed by the action of concentrated HNO_3, upon tin (p. 250).

It is insoluble in water and in all acids except concentrated sulphuric acid which dissolves it, forming unstable stannic sulphate:

$$SnO_2+2H_2SO_4 = Sn(SO_4)_2+2H_2O.$$

It is converted to soluble stannates by fusion with caustic alkalis:

$$SnO_2+2NaOH = Na_2SnO_3+H_2O.$$

It is an amphoteric oxide with predominant acidic properties; thus it is the anhydride of α-stannic acid, H_2SnO_3, and β-stannic acid (or metastannic acid), $H_2Sn_5O_{11}, 4H_2O$.

It is known in commerce as putty powder, and finds use as a polishing medium. It is used to make the white glazes for tiles, milk-glass shades, etc.

There is no carbonate of tin.

Stannous chloride, $SnCl_2$, is prepared by dissolving tin in hot concentrated hydrochloric acid: $Sn+2HCl = SnCl_2+H_2$; the solution, on evaporation and cooling, deposits transparent crystals of the dihydrate, $SnCl_2, 2H_2O$, known as *tin salt.* It dissolves in water, but the solution turns turbid due to the precipitation of stannous oxychloride by hydrolysis: $SnCl_2+HOH \rightleftharpoons Sn(OH)Cl+HCl$.

The hydrate decomposes on heating, giving off hydrogen chloride, and hence the *anhydrous chloride* is made by heating in a stream of hydrogen chloride.

Stannous chloride is a powerful reducing agent; thus it reduces mercuric chloride to mercurous chloride or to mercury, ferric chloride to ferrous chloride, and cupric chloride to cuprous chloride:

$$2HgCl_2+SnCl_2 = Hg_2Cl_2+SnCl_4\ ;Hg_2Cl_2+SnCl_2 = 2Hg+SnCl_4.$$

$$2FeCl_3+SnCl_2 = 2FeCl_2+SnCl_4;\ 2CuCl_2+SnCl_2 = Cu_2Cl_2+SnCl_4.$$

Zinc reduces $SnCl_2$ to spongy tin. $SnCl_2+Zn = ZnCl_2+Sn$.

The stannous chloride solution quickly becomes cloudy owing to atmospheric oxidation, unless it is kept with metallic tin and hydrochloric acid :

$$6SnCl_2 + 2H_2O + O_2 = 2SnCl_4 + 4Sn(OH)Cl.$$

Stannous chloride readily combines with iodine, forming $SnCl_2I_2$; the reaction lends itself to the volumetric estimation of tin by standard iodine solution :

$$SnCl_2 + I_2 = SnCl_2I_2.$$

In hydrochloric acid solution it forms the chlorostannous acid H_2SnCl_4, which gives such salts as $(NH_4)_2SnCl_4$.

Stannic chloride, $SnCl_4$, *a colourless fuming liquid,* b. p. 114°, is prepared by passing dry chlorine over molten tin in a retort and condensing the vapour of stannic chloride to a liquid (fig. 150).

$$Sn + 2Cl_2 = SnCl_4.$$

It is also obtained in detinning scrap tin plate by chlorine. Stannic chloride is also formed by distilling tin with mercuric chloride:

$$2HgCl_2 + Sn = SnCl_4 + 2Hg.$$

Stannic chloride dissolves in a small quantity of water, giving a clear solution, from which various hydrates may be crystallised out, including $SnCl_4$, $5H_2O$, known as butter of tin, which is used as mordant, especially for silk. The dilute solution is hydrolysed by water, precipitating basic chlorides and finally stannic hydroxide:

$$SnCl_4 + H_2O \rightleftharpoons SnCl_3(OH) + HCl;$$
$$SnCl_3(OH) + 3H_2O \rightleftharpoons Sn(OH)_4 + 3HCl.$$

With hydrochloric acid it forms chlorostannic acid, H_2SnCl_6, and with ammonium chloride it forms the double salt ammonium stannichloride, $(NH_4)_2SnCl_6$, which is used in dyeing under the name of *pink salt.* Stannic chloride is also soluble in alcohol and ether.

Stannous nitrate, $Sn(NO_3)_2$, is obtained by the action of dilute nitric acid upon tin. *Stannic nitrate* can be prepared by dissolving stannic hydroxide in nitric acid.

Stannous sulphate, $SnSO_4$, is obtained by dissolving stannous hydroxide in sulphuric acid; it is also formed when dilute sulphuric acid acts upon tin.

$$Sn + H_2SO_4 = SnSO_4 + H_2.$$

Stannic sulphate, $Sn(SO_4)_2$, is made by dissolving stannic hydroxide in H_2SO_4; it is hydrolysed by water.

Stannous sulphide, SnS, is made by heating tin with sulpur.. It is obtained as *brown* precipitate by passing H_2S through a solution of stannous chloride acidified with dilute HCl. $SnCl_2 + H_2S = SnS + 2HCl$.

It is soluble in conc. HCl, and in yellow ammonium sulphide forming ammonium thiostannate : $SnS + (NH_4)_2S_2 = (NH_4)_2\ SnS_3$.

The solution on acidification with dilute HCl, yields a *yellow* precipitate of stannic sulphide : $(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S$.

SnS is practically insolube in alkalis, and also insoluble in ammonium carbonate.

Stannic sulphide, SnS_2, is obtained as a yellow precipitate by passing hydrogen sulphide through dilute acid solution of stannic chloride,

$$SnCl_4 + 2H_2S \rightleftharpoons SnS_2 + 4HCl.$$

It is soluble in conc. HCl, and in yellow ammonium sulphide forming thiostannate, from which acids re-precipitate stannic sulphide. SnS_2 is insoluble in ammonium carbonate but dissolves in alkalis.

Mosaic gold or crystalline SnS_2, used for gilding, is obtained as golden yellow scales by heating a mixture of tin, sulphur and ammonium chloride in a retort. It is insoluble in all acids but dissolves in aqua regia or alkalis :

$$Sn+4NH_4Cl = (NH_4)_2SnCl_4+H_2+2NH_3.$$

$$2(NH_4)_2SnCl_4+2S = SnS_2+(NH_4)_2SnCl_6+2NH_4Cl.$$

Detection of tin : Dry tests.— (i) Tin componuds, when heated with sodium carbonate preferably in presence of potassium cyanide, on charcoal give white and malleable beads of tin; the beads react with hot concentrated HNO_3, yielding a white mass of metastannic acid and giving off brown fumes.

$$SnO_2+2KCN = Sn+2KCNO.$$

(ii) A borax bead which has been coloured pale blue by a trace of copper salt, turns ruby red in the reducing flame if a trace of tin compound is added.

Wet tests.— Solutions of $SnCl_2$ and $SnCl_4$ are used :

Reagent	Stannous salt	Stannic salt
(i) H_2S	Grey ppt. of SnS, soluble in conc. HCl and in yellow ammonium sulphide : practically insoluble in alkalis.	Yellow ppt. of SnS_2, soluble in conc. HCl, yellow ammonium sulphide and caustic alkalis.
(ii) $HgCl_2$ solution	White ppt. of Hg_2Cl_2 turning grey, if stannous salt be in excess.	No ppt., but gives a white to grey ppt. on reduction with Fe and HCl.
(iii) $FeCl_3$ and $K_3Fe(CN)_6$ soln.	Blue precipitate of Prussian blue.	No precipitate.

Lead

Occurrence, etc.— Native lead is occasionally found in traces, but the chief ore is **galena**, PbS, usually associated with *zinc blende.* Galena is found at Broken Hill (New South Wales), North America, Mexico, Spain, and in Northern Shan States in Burma. Galena usually contains about 0·01 to 0·1 per cent of silver. Less abundant, minerais are : *cerussite*, $PbCO_3$; *anglesite*, $PbSO_4$; *crocoisite*, $PbCrO_4$; *wulfenite*, $PbMoO_4$; *leadhillite*, $3PbCO_3.PbSO_4$; *lanarkite*, $PbO.PbSO_4$; *pyromorphite*, $3Pb_3(PO_4)_2$; $PbCl_2$; *matlockite*, PbClF. *Lead ochre*, PbO and *plattnerite*, PbO_2, are rare.

The lead smelting plant at Tundoo (Katrasgarh) in Bihar treats the lead ores obtained from Zawar (Udaipur) mines of Rajasthan.

Lead was known in ancient Egypt and Babylonia. It was largoly used by the Romans for cisterns, water pipes, etc.

Extraction—Lead is made from galena, PbS, by a process which involves (i) *concentration of the ore,* (ii) *roasting in air,* (iii) *smelting with coke, and* (iv) *refining*:

(i) **Concentration.**—Galena is separated from gangue and blende by oil-floation process, *vide* metallurgy of zinc (p. 421).

(i) **Roasting.**—The concentrated lead ore, mixed with some coal and lime (which acts as a flux), is roasted in a hot blast of air in a pot (fig. 181), whereby the lead sulphide is converted to lead oxide, which is *sintered* at the high temperature employed. $PbS+2O_2=PbSO_4$

$$2PbS+3O_2 = 2PbO+2SO_2.$$

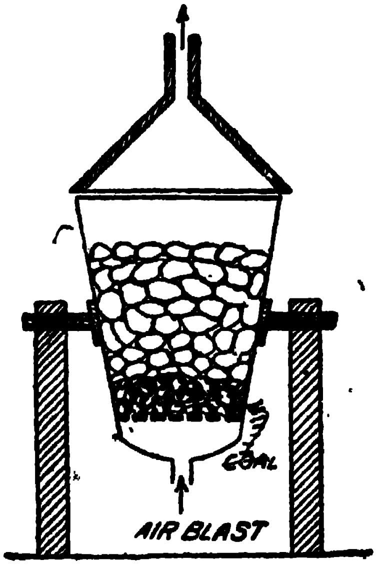


Fig. 181

The ore and the lime is charged on to the top of a coal fire first made on the grating and air is blown in through the bottom, when the charge is sintered into a large cake. The sintered mass is broken to pieces for charging into blast furnace. Any fumes produced in the operation is sucked away through a hood at the top.

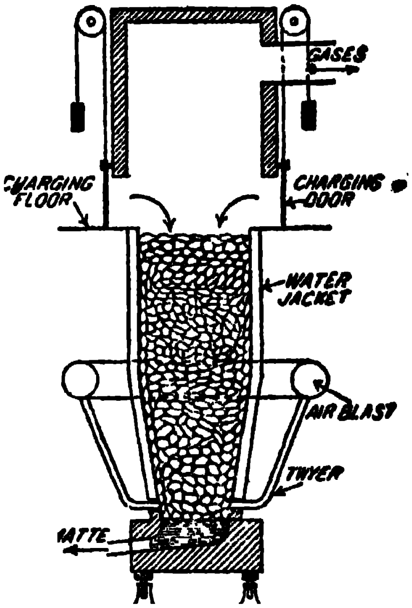


Fig. 182

(iii) **Smelting.**—The sintered lead oxide, mixed with coke and a flux of lime and iron oxide, is smelted in a small blast furnace (fig. 182). The air blast is forced through *tuyeres* at the base. The lead oxide is reduced by coke, and any unchanged lead sulphide by the iron formed by the reduction of the oxide in the charge.

$$PbO+C = Pb+CO;$$

$$2PbS+Fe_2O_3+3C = 2FeS+2Pb+3CO.$$

Any silicate ore is reduced by carbon in presence of lime: Lime reacts with silica, yielding a slag of calcium silicate. $PbSiO_3+CaO+C = CaSiO_3+Pb+CO.$

Molten lead and slag of iron sulphide and calcium silicate are withdrawn from the base of the furnace through separate tapping holes.

Lead was formerly extracted from *galena* by simple *roasting* and *smelting* in a *reverberatory furnace* (fig. 183); the process is to some extent still in use.

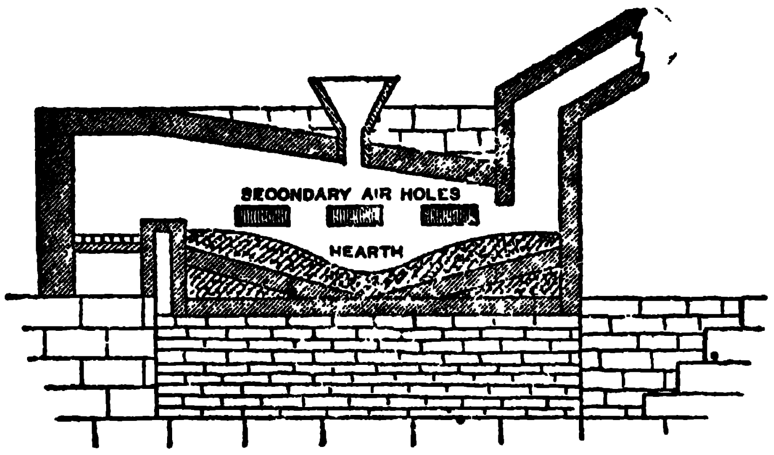


Fig. 183

(a) **Roasting.**—The ore is first *roasted in air* in the reverberatory furnace at a moderate temperature, when a *part of the galena* is oxidised to oxide and sulphate. $2PbS + 3O_2 = 2PbO + 2SO_2$; $PbS + 2O_2 = PbSO_4$.

(b) **Smelting.**—When about half the galena is oxidised, the air supply is cut off and the temperature is raised with the addition of a little lime to act as a flux. The charge smelts, when the unchanged lead sulphide reduces the lead oxide and sulphate, yielding metallic lead which is tapped out in the molten state. This is a *self-reduction process*, since the reduction takes place by lead sulphide itself.

$$PbS + 2PbO = 3Pb + SO_2; \quad PbS + PbSO_4 = 2Pb + 2SO_2.$$

(iv) **Refining.**—The crude lead contains *silver, copper, iron, zinc* arsenic, antimony, *bismuth,* and sulphur, which render the metal hard. *Softening* of the crude lead is effected by fusing it in a reverberatory furnace in contact with air, when the foreign metals except *silver* and *bismuth* are oxidised and removed as scum from the surface; arsenic and sulphur are eliminated as volatile oxides. The lead is then desilverised by any of the following processes; (i) *Pattinson's process* (p. 461); (ii) *Parke's process* (p. 462); (iii) *Betts' electrolytic process.*

Lead is refined in Betts' process by the electrolysis of a solution of lead silicofluoride, $PbSiF_6$, and hydrofluosilicic acid. H_2SiF_6, with a little gelatine, between *crude lead anode and pure lead cathode.* Lead dissolves from the anode and is deposited on the cathode. Silver, gold and bismuth are recovered as by products from the anode sludge.

Properties of lead.—(i) Lead is a very dense (sp. gr. 11·34), easily fusible (m. pt. 327·4°), bluish-grey metal with a bright lustre when freshly cut. It is malleable, soft and plastic, and *marks paper.*

(ii) It tarnishes in air by the formation of a superficial film of basic carbonate, which prevents further corrosion, and hence its use for roofing buildings. When melted in air, it is oxidised to *litharge,* PbO, and finally to *red lead,* Pb_3O_4.

$$2Pb+O_2 = 2PbO\,; \qquad 6PbO+O_2 = 2Pb_3O_4.$$

(iii) It is not attacked by pure air-free water; but *water containing dissolved oxygen corrodes the metal,* forming plumbous hydroxide which is slightly soluble and poisonous. The dissolution of lead by water is known as *plumbo-solvency.* $2Pb+O_2+2H_2O = 2Pb(OH)_2$.

This becomes a serious menace where lead piping is used for water supplies, since *lead is a cumulative poison.* But in the presence of mineral carbonate or sulphate in the water, the lead becomes coated with a protective layer of insoluble lead carbonate or sulphate, which arrests further corrosion.

Hence drinking water which is hard may be safely conveyed through lead pipes. Lead piping may also be used for conveying soft water previously treated with chalk or lime. Peaty water containing organic acids readily corrodes lead.

A blue line on the edge of gum is a symptom of lead poisoning, to which potters using lead glazes, and plumbers are likely victims.

because of insoluble layer of $PbCl_3$ or $PbSO_4$

(iv) It is insoluble in dilute HCl or dilute H_2SO_4. Boiling concentrated hydrochloric acid slowly attacks it: $Pb+2HCl = PbCl_2+H_2$. Hot concentrated sulphuric acid dissolves lead, giving off sulphur dioxide: $Pb+2H_2SO_4 = PbSO_4+2H_2O+SO_2$.

The action of HCl or H_2SO_4 is somewhat retarded by the coating of insoluble lead chloride or sulphate produced. It is scarcely attacked in the cold by sulphuric acid of less than 78% strength.

Dilute nitric acid readily dissolves lead:

$$3Pb+8HNO_3 = 3Pb(NO_3)_2+2NO+4H_2O.$$

Concentrated HNO_3 has little action upon lead, since lead nitrate is insoluble in it, and hence forms a protective coating.

In presence of air, lead is readily corroded by such weak acids as acetic and carbonic acid.

(v) It combines directly with chlorine and sulphur, when heated, to form respectively the chloride, $PbCl_2$ and the sulphide, PbS.

(vi) It is readily obtained as crystals by precipitation. A mass of arborescent crystals (*'lead tree'*) slowly deposits, when a zinc rod is hung in a solution of lead acetate:

$$Pb(CH_3COO)_2 + Zn = Zn(CH_3COO)_2 + Pb.$$

Uses of lead.—(i) Owing to its resistance to corrosion and cheapness it finds uses for *water pipes* and *cable coverings*, and as sheet lead for *roofing* buildings, and for *lining* vats in chemical industry, e.g., sulphuric acid chambers.

(ii) Lead is made harder by alloying with a second metal—some useful alloys are: *pewter* (Pb 20 : Sn 80), *solder* (Pb 50 : Sn 50), type metal (Pb 80 : Sb 15 : Sn 5), and *frary metal* (Pb 97 : Ba 2 : Ca 1) for bearings. An alloy with 1% tellurium is of general use where hard lead is needed; e.g., for water pipes. Hard lead with 10% antimony is used in pumps for corrosive liquids and in accumulator plates.

(iii) It also finds uses in making bullets (hardened by arsenic), white lead, lead tetraethyl (added to petrol as an anti-knock compound), etc.

Compounds of lead

Lead forms two series of compounds: *plumbus* compounds in which lead is divalent, *plumbic* compounds where the metal is quadrivalent. Plumbic compounds are readily hydrolysed, and difficult to obtain.

Oxides of lead.—Lead forms four oxides: Lead monoxide, PbO; Red lead, Pb_3O_4; Lead sesquioxide, Pb_2O_3; Lead dioxide, PbO_2.

(i) **Lead monoxide, litharge, massicot,** PbO, is obtained as a *yellow* powder, called *massicot,* by heating lead in air. When the massicot is fused, cooled and powdered, a *reddish-yellow* crystalline variety called *litharge,* is produced. It is commercially made by heating fused lead in air in a reverberatory furnace, and continuously skimming off the molten litharge floating on the surface; it is cooled, ground, and air-floated to remove unoxidised lead particles. It is a by-product in the cupellation of silver.

It is conveniently obtained in the laboratory by heating lead nitrate. $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$.

Any other oxide of lead is converted to PbO by heat above 600°.

Insoluble in water, and essentially a basic oxide, it reacts with acids, forming salts; but it also dissolves in hot caustic alkali, giving plumbites, and hence the amphoteric nature of the oxide.

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O \; ; \; PbO + 2NaOH = Na_2PbO_2 + H_2O.$$

The heated oxide is easily reduced by hydrogen, carbon or carbon monoxide. $PbO + H_2 = Pb + H_2O$; $PbO + C = Pb + CO$.

It is used as a 'drier' in paints and varnishes; in the preparation of lead salts, flint glass and glazes for pottery.

(ii) **Lead sesquioxide**, Pb_2O_3, a reddish-yellow powder, is formed by the action of sodium hypochlorite upon a *cold* solution of PbO in caustic potash. Its reactions are in accordance with the constitution, PbO, PbO_2.

$$2PbO + NaOCl = Pb_2O_3 + NaCl.$$

(iii) **Red lead, minimum,** Pb_3O_4, a scarlet powder, is made by calcining litharge (*vide supra*) for about 48 hours in a current of air in a muffle furnace—the temperature is kept within narrow limits, near 340°C. At temperature above 470° it decomposes into oxygen and litharge. $2Pb + O_2 = 2PbO$; $6PbO + O_2 \rightleftharpoons 2Pb_3O_4$.

Its chemical reactions suggest the constitution, $2PbO, PbO_2$. It reacts with cold concentrated or hot dilute nitric acid, forming lead nitrate and a precipitate of lead dioxide:

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O.$$

It reacts with hot concentrated HCl or H_2SO_4, giving off chlorine or oxygen. $Pb_3O_4 + 8HCl = 3PbCl_2 + 4H_2O + Cl_2$:

$$2Pb_3O_4 + 6H_2SO_4 = 6PbSO_4 + 6H_2O + O_2.$$

It finds uses in a red pigment; as a plumber's cement (mixed with linseed oil) for joining pipes, etc.; as a 'drier' in oil paints; in the preparation of flint glass and matches. It is used as an oxidising agent.

(iv) **Lead dioxide,** PbO_2, a chocolate-brown powder, is made: (a) by the action of hot dilute nitric acid upon red lead—the lead dioxide is filtered, washed and dried.

(b) by the action of an alkaline oxidising agent upon a lead salt. It is conveniently prepared by heating on water bath a solution of lead acetate with excess of bleaching powder. The brown precipitate of PbO_2 is stirred with hot dilute HNO_3 to remove any bleaching powder, filtered, washed with water and dried at 100°.

$$(CH_3COO)_2Pb + Ca(OCl)Cl + H_2O = PbO_2 + CaCl_2 + 2CH_3COOH.$$

It is formed on the positive plate during the charging of a lead accumulator.

It is insolube in water, in nitric acid, and in dilute HCl and H_2SO_4. It reacts with hot conc. HCl and H_2SO_4, giving off chlorine or oxygen respectively:

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2;$$

$$2PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O + O_2.$$

It dissolves in hot caustic soda or potash, forming plumbate:

$$PbO_2 + 2NaOH = Na_2PbO_3 + H_2O.$$

It is a powerful oxidising agent. It oxidises SO_2 spontaneously, forming lead sulphate: $PbO_2 + SO_2 = PbSO_4$.

A mixture of PbO_2 and sulphur inflames on trituration. A pink solution of permanganic acid is formed on heating a solution of manganous salt with concentrated HNO_3 and PbO_2.

$$2MnSO_4 + 5PbO_2 + 6HNO_3 = 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O.$$

Lead dioxide is stable up to 300°, but at higher temperatures it decomposes into PbO and oxygen. $2PbO_2 = 2PbO + O_2$.

It finds applications in the lead accumulator, in the preparation of matches and as an oxidising agent.

Lead hydroxide, $Pb(OH)_2$, is produced as white precipitate by adding sodium hydroxide (not in excess) to a solution of a lead salt. Insoluble in water, it dissolves both in acids and caustic alkalis.

Lead carbonate, $PbCO_3$, occurs in nature as cerussite and may be obtained as a white precipitate by adding $NaHCO_3$ to a solution of a lead salt—Na_2CO_3 precipitates basic lead carbonate $2PbCO_3, Pb(OH)_2$.

$$Pb(NO_3)_2 + 2NaHCO_3 = PbCO_3 + 2NaNO_3 + H_2O + CO_2.$$

White lead, basic lead carbonate, $2PbCO_3$, $Pb(OH)_2$.—The white lead was used as a pigment from ancient times. The best quality white lead is made by the so-called *Dutch process* (actually mentioned by Theophrastos in 300 B.C.) which is based on the corrosion of lead in presence of air and carbon dioxide. The process is carried out in earthenware pots (fig. 184) provided with shoulders from which are suspended on grids, strips of *highly purified* lead. The pots contain *vinegar* (a solution of 3% acetic acid) with which the strips of lead do not come in direct contact. Several pots are arranged on a thick bed of spent tan-bark (available at leather works) and covered with planks. Alternate layers of bark, pots and planks are built up until the shed is full and then allowed to stand for 4 to 5 weeks. The fermentation of the bark produces carbon dioxide and keeps the pots warm so that the acetic acid vaporises, and in presence of air and moisture attacks the lead, forming basic lead acetate which is converted to the basic carbonate by the carbon dioxide—the acetic acid set free again entering into the reaction.

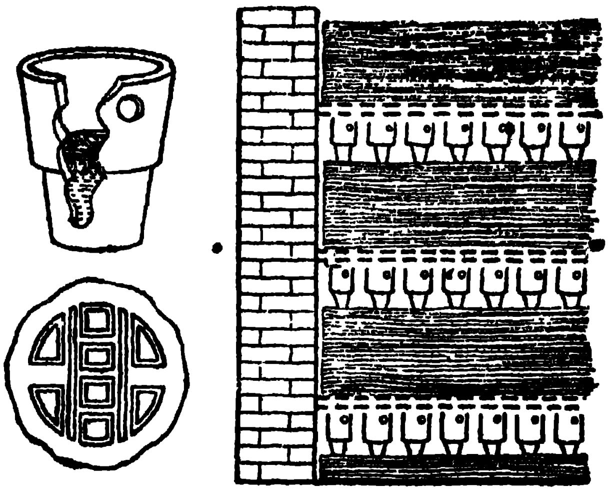


Fig. 184

The following cycle of reactions probably takes place :

$2Pb+O_2+2H_2O = 2Pb(OH)_2$; $Pb(OH)_2+2HAc = Pb(Ac)_2+2H_2O$.

$2Pb(Ac)_2+Pb(OH)_2 = 2Pb(AC)_2, Pb(OH)_2$.

$2Pb(Ac)_2, Pb(OH)_2+2H_2O+2CO_2 = 2PbCO_3,Pb(OH)_2+4HAc$.

HAc stands for acetic acid CH_3COOH, where $Ac = CH_3COO'$.

At the end of 4 to 5 weeks the strips become covered with a crust of white lead; this is stripped off, washed with water, ground and dried in vacuum driers.

Because of its very great covering power, it is extensively used as pigment as the basis for many white and coloured paints—mixed with linseed oil, it is extensively used as a white paint but it suffers from two defects : it is poisonous, and it gradually darkens due to the formation of brown-black lead sulphide by atmospheric hydrogen sulphide.

It has been displaced in part by the white pigments *lithopone* (p. 420), and zinc white (p. 424).

White lead of inferior quality may be precipitated by passing CO_2 into a solution of basic lead acetate, formed by boiling litharge with lead acetate solution (*Thenard process*).

White lead is prepared in **Carter process** by admitting air and carbon dioxide and spraying dilute acetic acid on atomised lead (made by injecting super-heated steam on the molten metal) in a revolving wooden drum—process is complete in two weeks. The product is ground, washed and dried. White lead is also made electrolytically.

Lead acetate, $Pb(CH_3COO)_2$, $3H_2O$, also called *sugar of lead* because it is sweet (but poisonous) in taste, is made by dissolving litharge or lead carbonate in hot dilute acetic acid and crystallising. It finds uses in medicine as an eye-wash, in dyeing and in making pigments, e.g., lead chromate (chrome yellow). Basic lead acetate solution, $Pb(CH_3COO)_2$, $Pb(OH)_2$, called Goulard's extract, is formed by boiling litharge with lead acetate solution, and is used as a lotion.

Plumbous chloride, lead chloride, $PbCl_2$, is obtained as a white precipitate by adding dilute HCl to lead nitrate solution: It is nearly insoluble in cold water (0·91 per cent), but more soluble in boiling water (3·2 per cent), from which it separates in needles on cooling. It dissolves in hot concentrated HCl.

$$PbCl_2 + 2HCl \rightleftharpoons H_2PbCl_4$$

Plumbic chloride, $PbCl_4$, *a heavy yellow oil,* is formed by the action of cold concentrated sulphuric acid upon ammonium plumbichloride:

$$(NH_4)_2PbCl_6 + H_2SO_4 = (NH_4)_2SO_4 + 2HCl + PbCl_4.$$

Ammonium plumbic chloride is precipitated by adding ammonium chloride to a solution prepared by dissolving lead dioxide in ice-cold concentrated HCl and saturating with chlorine.

$$PbO_2+4HCl \rightleftharpoons PbCl_4+2H_2O; \qquad PbCl_4+2HCl = H_2PbCl_6.$$
$$H_2PbCl_6+2NH_4Cl = (NH_4)_2PbCl_6+2HCl.$$

It rapidly decomposes at room temperature into $PbCl_2$ and chlorine, and is readily hydrolysed into PbO_2 and HCl.

Lead nitrate, $Pb(NO_3)_2$, is made by dissolving metallic lead, the oxide, or the carbonate in hot dilute nitric acid and crystallising the solution, when it is deposited in milky-white crystals. It is decomposed by heat:

$$2Pb(NO_3)_2 = 2PbO+4NO_2+O_2.$$

Lead sulphate, $PbSO_4$, is obtained as a heavy white precipitate by adding dilute H_2SO_4 to a solution of a lead salt.

It is slightly soluble in water (1 in 12,000) and practically insoluble in a mixture of dilute H_2SO_4 and alcohol (1 in 36,000). It dissolves in hot conc. H_2SO_4, and in hot ammonium acetate solution. Lead is estimated gravimetrically as $PbSO_4$.

Lead sulphide, PbS, occurs naturally as *galena.* It is precipitated as a black mass by passing H_2S through a solution of a lead salt. Lead burns in sulphur vapour, yielding lead sulphide. It is insoluble in yellow ammonium sulphide, but dissolves in boiling dilute HNO_3. It also dissolves in hot conc. HCl.

Detection of lead.— (i) When a lead compound is heated with sodium carbonate on charcoal, a soft malleable bead of lead (which marks paper), surrounded by a yellow incrustation, is obtained.

(ii) Dilute HCl gives with a solution of a lead salt a white precipitate of $PbCl_2$, which dissolves in boiling water but separates out again in needles on cooling.

(iii) With a solution of lead salt potassium iodide solution gives a yellow ppt. of PbI_2, which dissolves in boiling water, but separates on cooling in golden yellow plates. $Pb(NO_3)_2+2KI = PbI_2+2KNO_3$.

(iv) Potassium chromate solution, when added to solution of a lead salt, gives a yellow precipitate of lead chromate, insoluble in acetic acid.

$$Pb(NO_3)_2+K_2CrO_4 = PbCrO_4+2KNO_3.$$

Exercises

1. What is the chief natural source of aluminium, and how is the metal extracted from it? State the properties and uses of the metal. What reactions occur between (*a*) aluminium and ferric oxide, (*b*) aluminium and potash? How would you prepare anhydrous aluminium chloride, and alum from aluminium scrap? *Punjab* '51.

2. What is an alum? How is potash alum produced industrially? State its applications. Explain what happens when (*a*) sodium carbonate, (*b*) caustic soda, (*c*)ammonia is added to a solution of (i) aluminium chloride, (ii) zinc chloride.

3. How does tin occur in nature? How is the pure metal extracted from it? Mention the chief uses of the metal and its compounds. State what happens when tin is attacked (*a*) by nitric acid, (*b*) by hydrochloric acid, and (*c*) when exposed for a long time at low temperature. Compare the merits and demerits of tinning and galvanisation.

4. What is the chief natural source of lead, and how is the metal obtained from it? Give an account of a process for the desilverisation of lead. Discuss the solvent action of water upon lead. *Calcutta* '48.

5. Starting with metallic lead, how would you prepare; litharge, red lead, and lead dioxide? By what tests would you distinguish between these oxides? Describe the Dutch process for the preparation of white lead. Mention its uses. *Calcutta* '57.

6. Describe and explain what happens when; (*a*) a mixture of alumina and coke is heated in chlorine, (*b*) sodium nitrate solution is heated with aluminium dust and caustic soda, (*c*) sodium aluminate solution is shaken with ammonium chloride, (*d*) chlorine is passed over molten tin scrap, (*e*) a hot solution of ferric chloride is treated with stannous chloride solution, (*f*) lead dioxide is heated with concentrated sulphuric acid, (*h*) fused argentiferous lead is allowed to cool, (*i*) a mixture of coke and alumina is haeted in nitrogen.

7. How would you prepare (*i*) lead dioxide, (*ii*) crystals of lead nitrate, from red lead? State the effect of heat on them. What is the action of hydrochloric acid on (*i*) red lead, (*ii*) lead nitrate?

XXXII

Copper, Silver and Gold

Group IB of the periodic classification contains the coinage metals, copper, silver, and gold.

	At. no.	At. wt.	At. vol.	Density	M. pt. °C	B. pt. °C
Copper	29	63·57	7·1	8·94	1083·0	2310
Silver	47	107·88	10·3	10·47	960·5	1955
Gold	79	197·20	10·2	19·50	1063·3	2610

Occurrence.— Native copper is found in enormous masses in the region of Lake Superior in Canada, in Sweden, in Siberia and in Ural mountains. The chief minerals of copper are **chalcopyrite** or **copperpyrites** Cu_2S, Fe_2S_3; *chalcocite* or *copper glance*, Cu_2S; *cuprite* or *red copper ore*, Cu_2O; *tenorite* or *melaconite*, CuO; *malachite*, $CuCO_3$, $Cu(OH)_2$; *azurite*, $2CuCO_3$, $Cu(OH)_2$; *brochantite*, $CuSO_4$, $3Cu(OH)_2$; *atacamite*, $CuCl_2$, $3Cu(OH)_2$; *chrysocolla*, $CuSiO_3,2H_2O$.

The chief copper-producing regions are: Montana, Arizona, Canada, Japan, Russia, Rhodesia, Germany, Congo, Spain, and Chile. India is not rich in copper ore—the deposit of copper pyrites in Singhbhum, Bihar, is worked up at Ghatsila.

The sulphide ore alone accounts for about 75 p.c. of the world production.

Extraction of copper.—Native copper is smelted with a flux and then refined. Oxide and carbonate ores are roasted and then smelted with coke and flux, when crude copper is produced:

$$CuCO_3 = CuO + CO_2; \qquad CuO + C = Cu + CO.$$

By far the greater portion of copper is, however, made from the sulphide ore, copper pyrites, though its copper content is usually less than 2 per cent. The process involves the following steps:

(i) **Concentration by oil-floation process.**—The ore (chalcopyrite) is crushed and finely pulverised. The ore pulp is then suspended in water to which the flotation reagents, viz., *lime*, *pine oil* and *sodium xanthate*, have been added, and agitated with air. The copper-bearing particles collect in the froth formed on the surface of the liquid and are removed; the siliceous gangue is wetted by water and sinks to the bottom of the vessel (fig. 185). The ore concentrate in the froth is dewatered, filtered and dried.

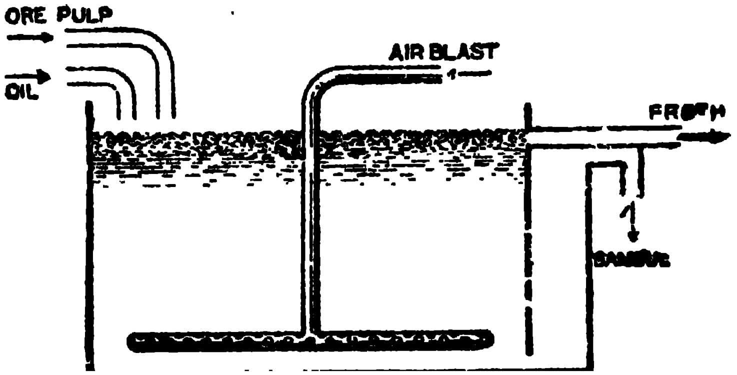


Fig. 185

(ii) **Roasting.**—The dried ore concentrates are partially roasted in a current of hot air in a multiple-hearth roaster (p. 421), when any arsenic present in the ore is volatalised as oxide, and *the baser metal iron*, which is more readily oxidised than copper, is partially converted to ferrous oxide. Any cuprous oxide that may be formed reacts with some of the unchanged ferrous sulphide with the formation of cuprous sulphide: $Cu_2O+FeS = Cu_2S+FeO$.

$$Cu_2S,Fe_2S_3+4O_2 = Cu_2S+2FeO+3SO_2.$$

A large proportion of sulphur is burnt out during roasting, leaving enough to hold all the copper and a portion of iron in combination as sulphides during the smelting operation.

The sulphur dioxide formed may be utilised in making sulphuric acid.

(iii) **Smelting**— Smelting is carried out either in a reverberatory furnace (for low grade sulphide ores) or in a blast furnace. The roasted ore is mixted with some unroasted ore and silica (which acts as a flux) and smelted on the hearth of a long reverberatory furnace which is fired by injecting coal dust and air within. The ferrous oxide is fluxed by silica, yielding a slag of liquid ferrous silicate, which floats, forming an immiscible layer, on the surface of the fused mixture of cuprous sulphide and unchanged ferrous sulphide known as **matte**:

$$FeO+SiO_2 = FeSiO_3.$$

The slag is run off and the matte transferred to a converter. The matte contains 40-45% copper, 30-35% iron, and about 25% sulphur.

The blast furnace (fig. 185) *smelting* is suitable for high grade lump ore only. The charge of partially roasted ore, mixed with some coke to act as a fuel and a flux of silica, is fed in at the top of a small water-jacketted blast furnace and air is forced in through tuyeres at the base. The charge is smelted, producing slag and matte, which run out from the bottom of the furnace into a settler, where they separate into the top layer of slag and the bottom layer of matte.

(iv) **Bessemerisation.**—The molten matte is poured into Bessemer converter (fig. 186) lined inside with magnesia bricks and a blast of air is turned on through ports in a pipe above the base of converter, and *not through the base, as in steel-making*. The ferrous sulphide is *selectively* oxidised to ferrous oxide before the cuprous sulphide gets oxidised. Correct amount of silica is added to react with the ferrous oxide to form a slag. The flame issuing from the converter is green so long as the elimination of iron is continuing.

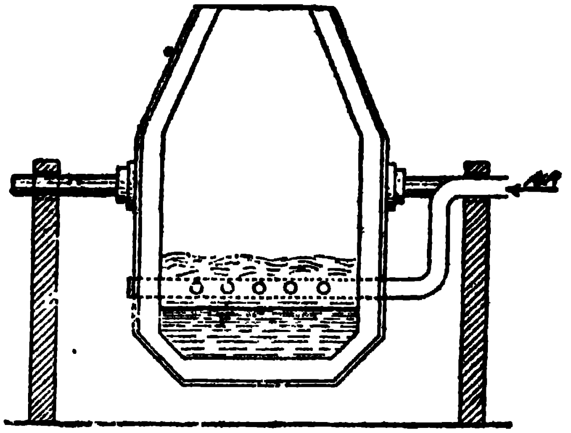


Fig. 186

When the green colour begins to fail, the air blast is stopped and the converter is tilted to pour the slag. It is again turned back to the blowing position and the air blast renewed, when the cuprous sulphide is partially oxidised to cuprous oxide which is reduced to metallic copper by the unchanged cupprous sulphide **by the process of self-reduction.**

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2;\ 2Cu_2O + Cu_2S = 6Cu + SO_2.$$

The process complete, the blast is stopped, the converter is tipped up and the crude copper **(blister copper)** poured out.

(v) **Refining of copper,**— (a) **Thermal refining.**—The blister copper contains 2-3% impurities, mainly iron and sulphur. It is refined by melting on the hearth of a reverberatory furnace in a current of air, when the chief impurities iron and sulphur are readily oxidised—the iron oxide collects on the surface as a scum and is removed; but the purified metal contains dissolved cuprous oxide which renders it brittle. The oxide is removed by sprinkling the surface with powdered anthracite and stirring the molten metal with a *pole of green wood* **(poling)**, when torrents of reducing gases are evolved, which reduce the oxide to metal. The correctly poled metal is known as *tough pitch copper*, and contains about 99·5% Cu.

(b) **Electrolytic refining.**— Thermally refined copper is pure enough for the manufacture of sheets, tubes, plates and some alloys, but it still contains many impurities, such as As, Sb, Fe, Ni, etc., which seriously lower its electrical conductivity. It also contains traces of the precious metals gold and silver. Copper of the highest purity suitable for electrical purposes is obtained by electrolytic refining.

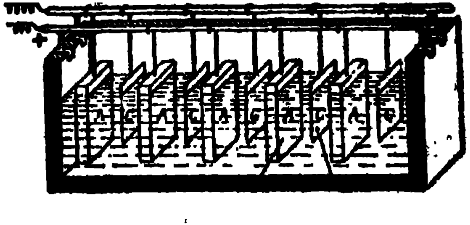


Fig. 187

Thick slabs (fig. 187) of thermally refined copper (which are made the anodes) are placed in between thin sheets of pure copper (which are the cathodes) in a bath of 15% copper sulphate solution containing 5-10% free sulphuric acid at about 50°. On electrolysis, copper dissolves from the anode, and is alone deposited on the cathode. The electrolytic copper is of 99·99% purity.

The *anode slime* contains valuable gold and silver, which are recovered.

Wet processes of copper extraction.— Low grade sulphide ores and the oxidised ores are suited for wet metallurgy. The ore is leached with a solvent, such as sulphuric acid, and the copper is obtained from the solution by precipitation with iron or by electrolysis.

(a) Iron precipitation process.— The low grade copper pyrites is piled up in moist heaps in air; the sulphides of iron and copper are converted to sulphates by slow atmospheric oxidation. The heaps are leached with water and copper is precipitated from the solution by scrap iron. The spongy precipitate of copper is melted down and refined. $CuSO_4+Fe = FeSO_4+Cu$.

The cupriferous burnt pyrites from the manufacture of sulphuric acid, is roasted with 10—15% common salt; this treatment, known as *chloridising roasting* converts the copper to soluble cupric chloride, which is leached with water; the copper is precipitated by scrap iron. $CuCl_2+Fe = FeCl_2+Cu$.

(b) Electrolytic methods.—The oxidised ores, such as *brochantite*, are leached with dilute sulphuric acid, and the solution of copper sulphate is electrolysed in cells fitted with anodes of *duriron* and cathodes of pure copper.

Properties.— (i) Copper is a rose-red metal with a high-conductivity for heat and electricity. It is soft, tough, malleable and ductile.

(ii) It slowly tarnishes in air, becoming covered with a brown film of oxide or sulphide, which on long exposure is converted to a *green patina of basic copper sulphate*, $CuSO_4,3Cu(OH)_2$.

When heated in air, it is converted to cupric oxide, CuO, but above 1100° cuprous oxide Cu_2O, is formed. $4CuO \rightleftharpoons 2Cu_2O+O_2$.

(iii) It is not attacked by water or steam even at a red heat; but it is slightly oxidised by steam at a white heat.

(iv) Less electro-positive than hydrogen, it is not attacked by cold solutions of non-oxidising acids, e.g., HCl or dilute H_2SO_4; the metal, however, dissolves slowly in conc. HCl or dilute H_2SO_4 in the presence of air: $2Cu+2H_2SO_4+O_2 = 2CuSO_4+2H_2O$;

$$2Cu+4HCl+O_2 = 2CuCl_2+2H_2O.$$

Hot conc. H_2SO_4 also dissolves it; it is also slowly attacked by boiling conc. HCl. It readily dissolves in nitric acid (p. 250).

$$Cu+2HSO_4 = CuSO_4+2H_2O+SO_2\ ;\quad 2Cu+8HCl = 2H_3CuCl_4+H_2.$$

(v) It combines directly, when heated, with chlorine and sulphur, to form respectively the chloride, $CuCl_2$, and the sulphide, CuS.

(vi) It dissolves in ammonium hydroxide in the presence of air, yielding a deep solution. It is attacked by fused alkali forming cupric oxide.

(vii) It displaces less electro-positive metals, such as silver, from their salts, but is itself deposited from its solutions by more electro-positive metals, such as iron and zinc:

$$2AgNO_3+Cu = 2Ag+Cu(NO_3)_2\ ;\quad CuSO_4+Zn = Cu+ZnSO_4.$$

Uses of copper.—(i) On account of its very high electrical conductivity, it is largely used for *telegraph* and *telephone wires, power lines,* and also for *electrical machinery. Copper for electrical purposes must be extremely pure.*

(ii) Owing to its high thermal conductivity coupled with resistance to corrosion by air and steam at high temperature, it is employed in *locomotive fire-boxes, for steam pipes, cooking utensils*, and also for roofing buildings.

(iii) It is used in electroplating and electrotyping (p. 129).

(iv) In making alloys—the alloy is made by adding the other metal to molten copper in a reducing atmosphere. Alloying improves mechanical properties of copper. Copper-base alloys are resistant to corrosion. Brass can be cast, drawn and stamped. Bronze has high tensile strength—besides tin, casting bronze contains some lead and zinc. Few non-ferrous alloys are :

ALLOY	COMPOSITION	USES
(i) Brass	Cu 70 Zn 30	Utensils, castings.
(ii) Delta metal	Cu 55 Zn 40 Fe 5 Resistant to sea water	Ship's propellors, valves, and bearings.
(iii) German silver	Cu 50 Zn 30 Ni 20	Utensils and in arts.
(vi) Bronze	Cu 90 Sn 10	Utensils.
	Bell metal Cu 80 Sn 20	Coins (Cu 95 Sn 4 Zn 1); Statues (Cu 90 Sn 5 Zn 4 Pb 1)
(v) Phosphor bronze	Cu 85 Sn 10 Pb 4 P 1 Hard, tough and elastic; withstands abrasion.	Aerial wires and suspension wires; valves, bearings.
(vi) Silicon bronze	Cu 97·5 Sn 1 Zn 1 Si 0·5	Telegraph wires.
(vii) Gun metal	Cu 88 Sn 10 Zn 2	
(viii) Aluminium bronze	Cu 90 Al 10 Golden yellow colour.	Statues, photoframes, coins, and paints.
(ix) Monel metal	Cu 30 Ni 67 Fe & Mn 3 Rust & acid proof.	Turbine blades, pumps, chemical apparatus.

Compounds of Copper

Copper forms two series of compounds : *cuprous* compounds where copper is univalent, and *cupric* compounds where the metal is divalent. Cuprous salts are generally *colourless* and insoluble in water, *e.g.*, CuCl, whereas the cupric salts are usually soluble in water and *blue* or *green* in colour, *e.g.*, blue vitriol. Most cuprous salts readily oxidise in air to the cupric state.

Cuprous oxide, Cu_2O, a *red powder*, is formed by the partial reduction of a cupric salt in alkaline solution. Red cuprous oxide is pricipitated by boiling copper sulphate solution with sodium carbonate and sodium sulphite:

$$2CuSO_4 + 2Na_2CO_3 + Na_2SO_3 = Cu_2O + 3Na_2SO_4 + 2CO_2.$$

But it is usually made by reducing hot Fehling's solution with glucose.

About 5 gms. of glucose in aqueous solution is added to a litre of *boiling* Fehling's solution; a yellow precipitate, perhaps of cuprous hydroxide, $Cu(OH)$, is first deposited, which readily turns to bright red cuprous oxide. This is filtered, washed with hot water and alcohol, and dried in a vacuum desiccator. This process is used in estimating sugar.

Fehling's solution is obtained as a *deep blue solution* by mixing equal volumes of two solutions, one containing 69 gms. of copper sulphate crystals in a litre, and a drop of H_2SO_4 to prevent hydrolysis, and the other 350 gms. of Rochelle salt (sodium potassium tartrate) and 100 gms. of caustic soda per litre.

Cuprous oxide is formed by strongly heating cupric oxide with copper powder: $CuO + Cu = Cu_2O$.

It is the stable oxide of copper at high temperatures, but when heated in air below 1000°, it is converted to cupric oxide; hydrogen reduces it to the metal. Insoluble in water, it dissolves in concentrated HCl, forming a colourless solution of cuprous chloride or the complex acid. H_2CuCl_3: $Cu_2O + 6HCl = 2H_2[CuCl_3] + H_2O$.

It dissolves in strong ammonia to a colourless solution if air is excluded, otherwise a blue solution results. It reacts with dilute sulphuric acid, depositing metallic copper.

$$Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O.$$

It readily dissolves in nitric acid with evolution of nitric oxide:

$$3Cu_2O + 14HNO_3 = 6Cu(NO_3)_2 + 2NO + 7H_2O.$$

It imparts a deep red colour to glass, and hence its use in making *ruby glass.*

Cupric oxide, *black oxide of copper,* CuO, is made commercially by heating *malachite,* native copper carbonate. It is also made by heating copper scale, the scourings of copper sheets, to redness.

$$CuCO_3,Cu(OH)_2 = 2CuO + H_2O + CO_2; \quad 2Cu + O_2 = 2CuO.$$

Insoluble in water, it readily dissolves in dilute acids, giving blue solutions of cupric salts; e.g., $CuO + H_2SO_4 = CuSO_4 + H_2O$.

It decomposes when heated above 1100°, into cuprous oxide and oxygen: $4CuO \rightleftharpoons 2Cu_2O + O_2$. It is chiefly used for colouring glass and glaze green or blue.

Oxides of copper are readily reduced to metal when heated in contact with carbon, carbon monoxide or hydrogen: $CuO + C = Cu + CO$.

Cupric Hydroxide, $Cu(OH)_2$, is formed as a light blue precipitate by adding excess of caustic soda to a solution of a cupric salt; it is insoluble in caustic alkali, but *soluble in excess of ammonia giving a deep blue solution of cupritetraammine* hydroxide: $Cu(OH)_2 + 4NH_4OH = [Cu(NH_3)_4](OH)_2 + 4H_2O$.

Cupric Carbonate.—The normal carbonate, $CuCO_3$, does not exist, but various basic salts are known, e.g., *azurite,* $2CuCO_3$, $Cu(OH)_2$ (deep blue); *malachite,* $CuCO_3.Cu(OH)_2$ (bright green). Basic copper carbonate is obtained as a green precipitate by adding sodium carbonate to a solution of copper sulphate.

Cuprous carbonate and hydroxide are unknown.

Cuprous chloride CuCl or Cu_2Cl_2, is prepared by dissolving a mixture of cupric oxide and copper turnings in boiling concentrated hydrochloric acid, and then pouring the colourless solution into a large volume of cold water (containing a little sulphur dioxide to avoid oxidation) when a white precipitate of cuprous chloride is thrown down: $Cu + CuO + 2HCl = 2CuCl + H_2O$.

It may also be obtained as a white precipitate by passing sulphur dioxide through a solution containing copper sulphate and sodium chloride until the solution smells strongly of SO_2.

$$2CuSO_4 + 2NaCl + 2H_2O + SO_2 = 2CuCl + 2NaHSO_4 + H_2SO_4.$$

In both cases the precipitate is filtered, washed with cold air-free water, then with alcohol, finally with ether, and dried in a vacuum desiccator.

It is a *white* solid but is gradually oxidised to green basic *cupric* chloride, $CuCl_2.Cu(OH)_2.H_2O$, in moist air.

It is insoluble in water, but dissolves in concentrated hydrochloric acid, forming $H_2(CuCl_3)$, and in aqueous ammonia, giving $(H_2O.Cu.NH_3)Cl$ – the colourless solutions readily absorb oxygen, becoming green or blue respectively: $CuCl+2HCl = H_2[CuCl_3]$.

$$4CuCl+4HCl+O_2 = 2H_2O+4CuCl_2.$$

Both solutions absorb carbon monoxide, forming the unstable carbonyl compound, $CuCl,CO,2H_2O$. The ammoniacal solution gives a red precipitate of cuprous acetylide, Cu_2C_2, with acetylene (p. 337). Ammoniacal cuprous chloride solution is used in *gas analysis* in the absorption of oxygen, carbon monoxide and acetylene.

Cupric chloride, $CuCl_2$ is made in the anhydrous state as a brown mass by passing excess of chlorine over heated copper, or by heating the hydrate, $CuCl_2,2H_2O$, in hydrogen chloride gas at 150°.

Emerald-green crystals of the dihydrate $CuCl_2,2H_2O$, are obtained by dissolving cupric oxide in conc. HCl and crystallising the solution.

It decomposes at a red heat, giving cuprous chloride and chlorine: $CuO+2HCl = CuCl_2+H_2O$; $2CuCl_2 = 2CuCl+Cl_2$.

It is very deliquescent, and is soluble in water and alcohol. The concentrated aqueous solution is *green* in colour, the dilute solution *blue*—the colour becomes *yellow* on the addition of conc. HCl.

It is readily reduced to cuprous chloride by boiling with copper turnings, or by treating with zinc dust, stannous chloride or SO_2:

$CuCl_2+Cu = 2CuCl$; $2CuCl_2+H_2SO_3+H_2O = 2CuCl+2HCl+H_2SO_4$.

$2CuCl_2+Zn = 2CuCl+ZnCl_2$; $2CuCl_2+SnCl_2 = 2CuCl+SnCl_4$.

Cupric Nitrate is obtained as blue deliquescent crystals of $Cu(NO_3)_2,3H_2O$ by dissolving metallic copper, the oxide, or the carbonate in dilute nitric acid, and crystallising the solution.

Copper sulphate, blue, vitriol, $CuSO_4,5H_2O$.—Blue vitriol is made (i) by spraying dilute sulphuric acid on to scrap copper packed in a lead-lined tower up which a current of air is sent; copper dissolves in presence of air, forming copper sulphate:

$$2Cu+2H_2SO_4+O_2 = 2CuSO_4+2H_2O.$$

The solution is circulated by means of a pump until sufficiently concentrated and then left for crystallisation in a vat, when crystals of blue vitriol deposit.

(ii) by heating scrap copper with sulphur, and then roasting the mass in air the resulting sulphide in order to convert it to sulphate, which is finally leached with dilute sulphuric acid and crystallised.

$$Cu + S = CuS; \qquad CuS + 2O_2 = CuSO_4.$$

(iii) by the 'weathering' of copper pyrites which is first gently roasted to convert copper sulphide to sulphate; copper sulphate is leached out with water and crystallised.

Commercial copper sulphate contains isomorphous ferrous sulphate. It is purified by recrystallisation from water containing a little nitric acid, when the ferrous sulphate is oxidised to ferric sulphate which, not being isomorphous with copper sulphate, remains in solution.

On exposure to air the blue pentahydrate effloresces to give the trihydrate, and when heated at 100° it losses four molecules of water and forms the monohydrate, $CuSO_4,H_2O$; at about 250° it yields the colourless anhydrous salt, which rapidly absorbs moisture to give the blue pentahydrate, and *hence its use for detecting traces of water in gases and non-aqueous liquids.* Copper sulphate it completely decomposed at 750°, leaving a residue of cupric oxide.

Copper sulphate readily absorbs hydrogen chloride: $CuSO_4 + 2HCl = CuCl_2 + H_2SO_4$; the reaction may be used for removing HCl from other gases, such as sulphur dioxide.

Copper sulphate is toxic to lower organisms, and hence its use as a germicide and fungicide in agriculture, e.g., vines and potatoes are sprayed with Bordeaux mixture (a solution of copper sulphate mixed with slaked lime). It is also used in copper plating, in dyeing and calicoprinting, and for preserving wood and hides.

Copper sulphate reacts with potassium iodide solution, giving a *white precipitate of cuprous iodide.* CuI, (which may be filtered, washed, and dried as in preparation of CuCl) and quantitatively liberating iodine; the reaction is used in estimating copper:

$$2CuSO_4 + 4KI = 2K_2SO_4 + 2CuI + I_2.$$

Copper sulphate reacts with potassium cyanide giving a white precipitate of cuprous cyanide and evolving cyanogen gas—the cuprous cyanide dissolves in excess of KCN forming stable potassium cuprocyanide, $K_3[Cu(CN)_4]$.

$$2CuSO_4 + 4KCN = 2CuCN + (CN)_2 + 2K_2SO_4\ ;$$

$$CuCN + 3KCN = K_3[Cu(CN)_4].$$

Cupric Sulphide, CuS, is formed as a black precipitate by passing H_2S through an acid solution of a cupric salt. It is insoluble in dilute HCl and yellow ammonium sulphide, but is soluble in nitric acid.

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

In the moist state it is readily oxidised by air to give copper sulphate. It is less stable than cuprous sulphide, and loses sulphur on gentle heating.

$$2CuS = Cu_2S + S.$$

Cupric sulphide is formed by heating copper powder with excess of sulphur. Cuprous sulphide is a black solid produced when copper burns in sulphur vapour.

Detection of Copper.—Dry Tests.—(i) *Blow pipe test.*—A copper compound mixed with sodium carbonate and heated on charcoal in the reducing flame, yields a *red* mass of copper, which dissolves in HNO_3, giving off brown fumes, and forming a blue solution of cupric nitrate.

(ii) *Borax bead.*—Green when hot and blue when cold after heating in the oxidising flame; red in the reducing flame, especially after adding a trace of a tin salt.

(iii) *Flame test.*—Bluish green, especially after moistening with conc. HCl. before heating.

Wet Tests.— Reactions of the cupric salts : used a solution of cupric sulphate. (i) H_2S gives a back ppt. from an acidified (with dilute HCl) solution: the precipitate is soluble in hot dilute HNO_3. (ii) Ammonia gives a pale blue ppt.

of basic copper sulphate, which dissolves in excess of ammonia giving a *deep blue solution* (p. 230). (iii) Potassium ferrocyanide gives a chocolate precipitate of cupric ferrocyanide.

Silver

Occurrence.—Silver is found native in Norway, Peru and Canada. Important ores are : *argentite* or *silver glance*, Ag_2S; *stromeyerite* or *silver copper glance*, Ag_2S, Cu_2S; *pyrargyrite* or *ruby silver*, $3Ag_2S$, Sb_2S_3; *chlorargyrite* or *horn-silver*, AgCl. Most copper and lead ores, such as *copper pyrites* and *galena*, contain small quantities of gold and silver. The principal silver-producing countries are : Mexico, Peru, Ontario, Colorado, and Broken Hill in Australia.

Metallurgy.—The chief processes for the extraction of silver are: (i) **Leaching process :** In the modern cyanide process, the ore is finely ground in ball mills, and then leached with a dilute (0·4%) sodium cyanide solution—the sludge being agitated by a stream of air. Metallic silver, silver sulphide, and silver chloride all dissolve giving a solution of sodium argentocyanide:

$$4Ag + 8NaCN + O_2 + 2H_2O \rightleftharpoons 4Na[Ag(CN)_2] + 4NaOH.$$

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S\,;$$

$$AgCl + 2NaCN = Na[Ag(CN)_2] + NaCl.$$

The sodium suphide formed, which tends to reverse the reaction, is oxidised by air to sodium sulphate:

$$4Na_2S + 5O_2 + 2H_2O = 2Na_2SO_4 + 4NaOH + 2S.$$

The sodium argentocyanide solution is filtered from the sludge, and the silver precipitated from the solution by the addition of zinc or aluminium: $2NaAg(CN)_2 + Zn = 2Ag + Na_2Zn(CN)_4$.

This is filtered, washed, melted with a flux of nitre to oxidise away any excess of zinc, and then made into bullion.

The silver is also precipitated from the solution by sodium sulphide and the silver sulphide reduced by caustic soda solution and aluminium ingots.

$$2Na[Ag(CN)_2] + Na_2S = Ag_2S + 4NaCN$$

$$3Ag_2S + 8NaOH + 2Al = 6Ag + 3Na_2S + 2NaAlO_2 + 4H_2O.$$

In **Ziervogel process** the sulphide ore is roasted into soluble silver sulphate which is leached with water and the silver precipitated by copper. $Ag_2SO_4 + Cu = CuSO_4 + 2Ag$. The ore may be converted into silver chloride by roasting with common salt; the silver chloride is either leached with hot brine **(Augustin process)** and the silver precipitated with copper or with sodium thiosulphate solution **(Percy—Patera process)** and the silver precipitated as Ag_2S which is then reduced to the metal by Al and caustic soda :

$$AgCl + 2Na_2S_2O_3 = Na_3[Ag(S_2O_3)_2] + NaCl.$$

$$2Na_2[Ag(S_2O_3)_2] + Na_2S = 4Na_2S_2O_3 + Ag_2S.$$

(ii) **Lead process.**—When argentiferous lead ores (galena containing 0·01 to 0·1% Ag) is smelted alone or with added silver ore, or when a silver ore is smelted with lead, the whole of silver is separated and collected as an alloy of lead and silver. The silver it contains, is concentrated by Pattinson's or Parke's processes and the enriched argentiferous lead is then subjected to cupellation in order to remove the lead as oxide.

(a) **The Pattison's process** depends on the fact that when fused argentiferous lead (containing less than 2·25 p.c. silver which is present in the eutectic mixture) is cooled, crystals of lead continue to deposit (at a temperature below the freezing point, 327°, of lead, because of its depression by the dissolved silver) as the temperature falls, and the residual liquid alloy becomes increasingly rich in silver until the eutectic composition is reached, when lead and silver solidify together at the eutectic point, 303°.

The process is carried out in a row of 10 iron pots—the argentiferous lead being melted and allowed to cool at the central pot; crystals of lead that separate are removed by a ladle to a pot to the left, and the enriched liquid alloy to a pot to the right. This process of fractional crystallisation is repeated along the entire row of pots, when pure desilvered lead (containing 0·001% Ag) is finally obtained in a pot on the extreme left, and enriched silver-lead alloy in a pot on the extreme right. The 'rich alloy containing about 1% Ag only, is then cupelled.

In a modification known as **Luce-Rozan process** the argentiferous lead is melted and cooled by blowing steam through the fused metal and spraying cold water on the surface. When two-thirds of lead has solidified, the liquid (containing about 2% silver) is run off through a perforated plate and finally cupelled. The solidified lead is remelted and the process is repeated until the lead is practically free from silver.

(b) **The Parke s process** depends on the fact that when argentiferous lead is fused with zinc, (i) two immiscible liquid layers separate—an upper layer of zinc containing 1·2% of lead only, and a lower layer of lead containg 1·6% of zinc only, and (ii) any silver originally present in lead distributes itself between the two layers, such that its concentration in the zinc layer is 300 times that in the lead layer.

About 1% of zinc is added to molten argentiferous lead in iron pots containing some 25 tons; the mixture is stirred and allowed to cool. The argentiferous zinc solidifies and is skimmed off with a perforated ladle. The process is repeated until the lead contains about 0·0004% of silver. The desilvered lead contains a little zinc, which is removed as oxide by blowing steam through the molten metal.

The skimmings of silver-zinc alloy with mechanically adhering lead is heated with carbon to reduce any zinc oxide which may have been formed in a fire clay retort, when zinc distils off, leaving a residue of 10% Ag and 90% Pb, which is cupelled. This process is now used in preference to the Pattison's method.

Cupellation.—The enriched silver-lead alloy is subjected to cupellation, a process of more than 2000 years old. The process consists in blowing air over the surface of the molten alloy contained in a *cupel*, a shallow dish of bone ash or cement, placed on the hearth of a reverberatory furnace (fig. 188). The lead is oxidised to litharge, PbO, which fuses and is blown away by the air blast while silver remains unaffected. The last portions of litharge are absorbed by the porous cupel, when the bright *surface of silver flashes out,* indicating the end of the operation. The button of silver formed is 99·5% pure.

(iii) **Amalgamation process.**—The process has been in use in Mexico since 1557, but is now being gradually replaced by the cyanide method. The wet ore is finely crushed, mixed with about 5% common salt, and then well trodden by mules on a paved floor or *patio*, with successive additions of mercury and roasted pyrites, containing cupric and ferric sulphates. The salt and roasted pyrites, give cupric chloride, which reacts with silver sulphide, producing silver chloride, the latter being reduced to the metal by the mercury: $CuSO_4 + 2NaCl = CuCl_2 + Na_2SO_4$; $CuCl_2 + Ag_2S = CuS + 2AgCl$: $2AgCl + 2Hg = Hg_2Cl_2 + 2Ag$. The silver dissolves in the excess of mercury to form an amalgam.

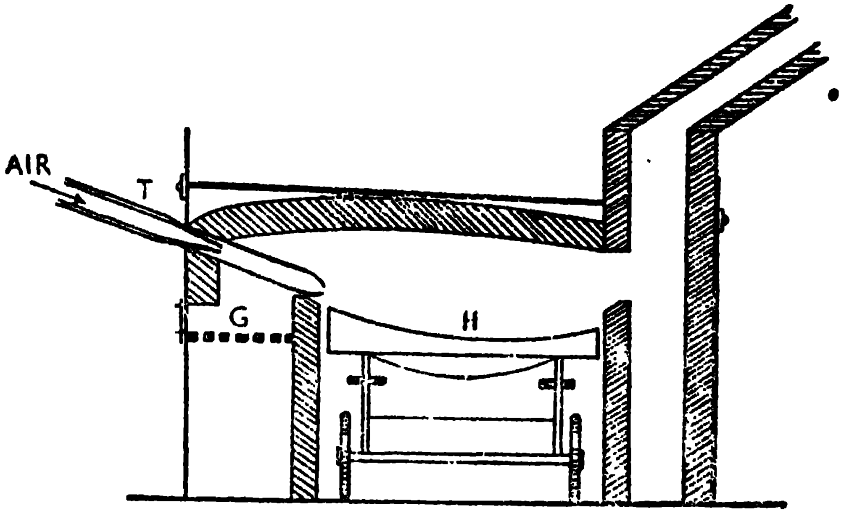


Fig. 188

The amalgam is separated by washing, and then distilled to recover the mercury. The residue of crude silver is then cupelled

(iv) **Electrolytic process.**—The anode slime formed in the electro-refining of copper, is an important source of silver. This is leached with a mixture of sulphuric acid and nitre to dissolve the copper, dried and then fused in a current of air to oxidise the base metals, which then form a slag—arsenious oxide volatilises. The molten metal is finally purified by fused nitre, and then cast into ingots which may contain 96% Ag, 2% Cu, and 2 per cent Au.

Parting of silver and gold.— The silver made by all the above methods invariably contains some gold. They are separated or 'parted' as follows :

(i) **Electrolytic parting.**— The ingots of crude silver are made the anodes in a bath of 2 to 5% silver nitrate solution with about 2% free nitric acid, the cathodes being sheets of pure silver. During electrolysis silver dissolves from the anodes and is deposited at the cathodes as crystals, which are brushed off, washed, melted and cast into bars. The silver so obtained is of 99% purity. The gold remains undissolved, and is collected as a spongy mass in bags round the anodes; this is melted into ingots. The gold ingots are then made the anodes in a hot solution of 4·7% auric chloride with about 10% hydrochloric acid, the cathodes being sheets of pure gold. Gold dissolves from the anodes and is deposited at the cathodes.

(ii) **Parting by acids.**—The crude silver containing less than 20% gold, is granulated and then treated with boiling concentrated sulphuric acid, when silver dissolves as silver sulphate, leaving a spongy residue of gold. The solution is diluted and the gold filtered off—silver is precipitated from the filtrate by scrap iron or copper. $Ag_2SO_4 + Fe = FeSO_4 + 2Ag$.

Properties of silver.—(i) Silver is a lustrous white metal capable of taking a high polish; tough, malleable and ductile, *it is the best conductor of heat and electricity.*

(ii) It tarnishes on exposure to air due to the formation of a black film of silver sulphide by the action of atmospheric hydrogen sulphide; the tarnishing may be prevented by alloying the metal with cadmium: $4Ag + 2H_2S + O_2 = 2Ag_2S + 2H_2O$.

It is not affected by oxygen, but when heated in air it melts without tarnishing, dissolving more than 20 times its own volume of oxygen which is

INTERMEDIATE CHEMISTRY

almost completely ejected during solidification; the phenomenon is known as the '**spitting of silver.**'

(iii) It is not attacked by water, by fused caustic alkalis or alkaline solutions, or by ammonia.

(iv) Less electro-positive than hydrogen, it is insoluble in dilute hydrochloric or sulphuric acids; but it dissolves in oxidising acids, hot conc. H_2SO_4 and nitric acid of all degrees of dilution:

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2;$$

$$Ag + 2HNO_3 = AgNO_3 + H_2O + NO_2.$$

Hot conc. HCl slowly attacks silver, forming silver chloride which is soluble in the concentrated acid. It is also attacked by gaseous hydrogen chloride.

(v) It combines directly, when heated, with sulphur and the halogens, to form respectively the sulphide, Ag_2S, and the halides.

(vi) It is displaced from its solution by all metals, except gold and platinum metals: $2AgNO_3 + Cu = Cu(NO_3)_2 + 2Ag$.

Uses of Silver.—It finds uses in the preparation of silver nitrate, ornaments and silver wares; in electroplating, in silver mirrors, and coins. Silver crucibles are used in alkali fusion. Colloidal silver is used in medicine.

Silver plating.— Articles of cheaper materials, usually of copper or German silver, are covered with a thin adherent film of silver by electro-deposition. The article to be plated is made the cathode in a bath of potassium argentocyanide solution, the anode being a plate of pure silver (p. 129).

Silver mirrors.—A mirror of silver on glass is made by reducing an ammoniacal solution of silver nitrate with glucose or tartaric acid.

Expt.—Silver nitrate solution is added to a solution of sodium potassium tartrate (Rochelle salt) in a clean test tube—the white, curdy precipitate formed is *just* redissolved in dilute ammonium hydroxide solution. On placing the test tube in a beaker of boiling water, a continuous film of bright silver is formed on the glass surface.

Oxidised silver.—'Oxidised' silver articles are made by dipping in a solution of sodium sulphide, in order to cover the surface with a pleasant greyish film of silver sulphide which protects the metal from tarnishing in air.

Silver alloys.— Silver is alloyed with copper, since the pure metal is too soft for coinage or jewellery. The proportion of silver in 100 parts of the alloy is called the **fineness.** Until 1919. British silver coin had a fineness of 925, i.e., 92·5% Ag and 7·5% Cu; but the standard is now reduced to 50 p.c. silver, the rest being nickel and a little copper.

The *assay* of silver is done by heating the alloy with lead on a bone ash *cupel* in a muffle furnace, which is only loosely closed, so as to admit air. The copper is converted to its oxide and dissolves in molten lead oxide, which is absorbed by the cupel.

Photography.—The fact that the halides of silver are sensitive to light is utilised in photography. When a photagraphic film which contains an emulsion of silver bromide in gelatin, is exposed to an object in light, an invisible image is thrown on the film by the lens of a camera, due to the incipient reduction of the silver halide upon which lights falls. The *latent image* thus produced is *developed* by immersing the exposed film in a solution of a reducing agent, such as potassium ferrous oxalate, which reduces the exposed silver halide to black metallic silver: $K_2Fe^{\cdot\cdot}(C_2O_4)_2 + AgBr = KFe^{\cdot\cdot\cdot}(C_2O_4)_2 + Ag + KBr$.

The developed image contains metallic silver and silver bromide. It is made stable to light by *fixing*, i.e., by dissolving out the unchanged silver bromide in a bath of sodium thiosulphate, also called 'hypo'; a *negative* is thus produced, in which the light and shade of the image are reversed. Developing and fixing are done in a dark room having a red light. $AgBr+2Na_2S_2O_3 = Na_3[Ag(S_2O_3)_2]+NaBr$.

A positive print is obtained by laying the negative on a printing paper, covered with an emulsion of silver chloride in gelatin, and then exposing for some minutes to sun light; the print is then developed and fixed as before. Fixation gives a disagreeable colour to the print, hence it is *toned*, i.e., given a richer colour, by immersing into solution of potassium aurichloride when some of the silver is replaced by gold: $3Ag+KAuCl_4 = Au+KCl+3AgCl$. Fixing and toning are done simultaneously.

Compounds of silver

Silver is univalent in its simple salts. Complex compounds of bivalent silver are known, *e.g.*, the anodic oxidation of silver nitrate in presence of pyridine yields the orange-red pyridine compound of argentic nitrate, $[Ag\text{-}4C_5H_5N]\ (NO_3)_2$, which is an oxidising agent and liberates iodine from potassium iodide. Silver salts are very sensitive to light.

Silver oxide, Ag_2O, is obtained as a dark-brown precipitate by adding caustic soda to a solution of silver nitrate—it is dried below 100°, since it gives off oxygen at higher temperatures and is completely decomposed at 300°. It has been used as a source of pure oxygen.

$$2AgNO_3+2NaOH = Ag_2O+2NaNO_3+H_2O.$$

It is very slightly soluble in water, but the moist silver oxide is alkaline to litmus, and is used as a base and as an oxidising agent in organic chemistry. It readily absorbs CO_2 forming silver carbonate. It dissolves in ammonia, producing the ammine hydroxide, $(Ag.2NH_3)OH$—the solution on exposure to air deposits the explosive silver nitride, Ag_3N, also called *fulminating silver.*

Silver carbonate, Ag_2CO_3, a light yellow powder, is precipitated by adding sodium carbonate to a solution of silver nitrate.

Silver chloride, AgCl, is formed as a white curdy precipitate by adding dilute HCl or a solution of a metallic chloride to a solution of silver nitrate; it is coagulated by boiling, filtered, washed with hot water and dried—it fuses at 455°. It may also be made by passing chlorine over silver at a dull red heat.

It is insoluble in water (solubility, 0·0002% only) and in dilute acids (including nitric acid). Its insolubility offers a method for the estimation of silver (or of chlorides). It is soluble in ammonia, and in solutions of sodium thiosulphate and of potassium cyanide:

$$AgCl+2NH_3 = [Ag(NH_3)_2]Cl; \qquad AgCl+2KCN = K[Ag(CN)_2]+KCl.$$
$$AgCl+2Na_2S_2O_3 = Na_3[Ag(S_2O_3)_2]+NaCl.$$

It also dissolves slowly in conc. HCl and in concentrated sodium chloride solution. *It darkens on exposure to light.*

Silver chloride is readily reduced to pure metallic silver:

(i) by fusion with sodium carbonate in a crucible, when a button of pure silver is formed, $4AgCl+2Na_2CO_3 = 4Ag+4NaCl+2CO_2+O_2$;

(ii) by heating in a current of hydrogen, $2AgCl+H_2 = 2Ag+2HCl$;

(iii) by boiling with a solution of caustic potash and glucose;

(iv) by placing it in contact with zinc or aluminium in dilute hydrochloric acid, $AgCl+H = Ag+HCl$. The precipitated slver from (iii) and (iv) is fused with sodium carbonate to form a button.

These methods are available for obtaining **pure silver** from **silver coin,** the latter is dissolved in hot dilute HNO_3, when copper nitrate and silver nitrate are formed. Silver is precipitated as silver chloride from the hot solution by a slight excess of dilute HCl, filtered, washed with hot water until free from acid, dried, and then reduced as above.

Silver nitrate, lunar caustic, $AgNO_3$, is prepared in transparent crystals by dissolving silver in hot dilute HNO_3 and concentrating the solution to crystallisation: $Ag+2HNO_3 = AgNO_3+NO_2+H_2O$.

It melts at 217° and may be cast into sticks. It is freely soluble in water—the solution slowly darkens on exposure to light. The solution gives brown precipitate of silver oxide, Ag_2O, with ammonium hydroxide solution, soluble in excess of the precipitant—the ammoniacal solution on evaporation yields the crystals of the ammine $[Ag.2NH_3]NO_3$.

$$2AgNO_3+2NH_4OH = Ag_2O+2NH_4NO_3+H_2O.$$

$$Ag_2O+4NH_4OH = 2(Ag.2NH_3)OH+3H_2O.$$

Solid silver nitrate however absorbs ammonia gas, forming the compound $AgNO_3,3NH_3$. It reacts with potassium cyanide solution, forming potassium argento cyanide (p. 129).

$$AgNO_3 + 2KCN = K[Ag(CN)_2] + KNO_3$$

It exercises a strong corrosive action upon organic tissues, which it stains black owing to its reduction to the metal in fine state of division. It decomposes at a dull red heat, about 500°, to silver nitrite and finally to the metal thus:

$$2AgNO_3 = 2AgNO_2+O_2\,; \quad 2AgNO_2 = 2Ag+2NO+O_2.$$

But its decomposition point is much higher than that of copper nitrate, a fact which provides a method for preparing silver nitrate from a **silver coin.** The coin is dissolved in HNO_3, and the solution is evaporated to a residue of $AgNO_3$ and $Cu(NO_3)_2$, which is heated to 250°, then treated with water and filtered from the insoluble copper oxide—the filtrate is crystallised for silver nitrate.

$$2Cu(NO_3)_2 = 2CuO+4NO_2+O_2.$$

It is used as a caustic in surgery under the name of *lunar caustic*; in the preparation of silver halides used in photography; as a reagent in the laboratory; in silver plating and silver mirrors; for making linen.

Silver sulphate, Ag_2SO_4, is formed by heating finely divided silver with concentrated sulphuric acid. $2Ag+2H_2SO_4 = Ag_2SO_4+2H_2O+SO_2$.

It is sparingly soluble in water. It is reduced to the metal by strong heat:

$$Ag_2SO_4 = 2Ag+SO_2+O_2.$$

Silver sulphide, Ag_2S, is precipitated as a black substance by the action of H_2S upon a solution of a silver salt. It is also formed by heating silver with sulphur or in hydrogen sulphide. It is insoluble in dilute acids, sodium thiosulphate and ammonia but dissolves in potassium cyanide solution—*hence the use of cyanide in brightening the surface of tarnished silver wares.*

Detection of Silver.—Dry test: When a silver compound is heated with sodium carbonate on charcoal, a lustrous white malleable bead results, this is readily soluble in nitric acid.

Wet tests.— A solution of silver nitrate is used : (i) Dilute HCl gives a white curdy precipitate of silver chloride, which is insoluble in nitric acid but readily soluble in ammonia.

(ii) Potassium chromate solution gives a red precipitate of silver chromate, which is insoluble in acetic acid : $2AgNO_3+K_2CrO_4 = Ag_2CrO_4+2KNO_3$.

Gold

Gold is the most anciently known of metals. Gold ornaments have been found in the neolithic remains of ancient Egypt and Babylonia.

Occurrence.—Gold is widely distributed in nature. It usually occurs *native* either in alluvial sand and gravel deposits or in quartz veins. Traces are found in pyrites. It is found in small amounts as telluride, AuTe.

The richest gold fields are in Africa, especially the Transvaal. Other important sources are North America, Australia, Canada, Russia, Korea, Hungary, and India—the Kolar gold fields in Mysore State deserve special mention.

Gold occurs in traces of 0·01 to 0·05 mg. per cu. m. in seawater.

Metallurgy.—(i) Washing and amalgamation process.—Native gold occurs in *alluvial sand* and *gravel deposits* as grains or as nuggets. It is extracted from the deposits by washing with water in agitating pans or in sluices—the hard deposits are broken up by powerful jets of water (*hydraulic mining*) projected on to them. The running water carries the grains of gold together with much sand and clay, etc., in suspension. The suspension passes through long slightly inclined wooden trough with battens across the bottom when the light worthless material is carried away and the heavy gold (density 19·43) particles sink to the bottom of the troughs and caught by battens.

The hard auriferous quartz and rocks are crushed by jaw crushers and then powdered in stamps or ball mills. A stream of water carrying the slime from mills is passed over amalgamated copper plates which arrest the gold particles, while the gangue passes off. The amalgam is scraped out and distilled in iron retorts, and the residue finally cupelled to obtain the gold.

(ii) Cyanide process (MacArthur and Forrest process). —The auriferous rocks are usually treated by the cyanide process. The ore is finely crushed in stamp mills and placed in vats with false bottoms and percolated with dilute (0·15 per cent) sodium cyanide solution —sometimes the slimes are agitated in tanks with the cyanide solution. The cyanide solution is made alkaline by adding lime. Gold slowly reacts with sodium cyanide in presence of air, forming sodium aurocyanide which passes into solution:

$$8NaCN+4Au+2H_2O+O_2 = 4Na[Au(CN)_2]+4NaOH.$$

After settling or filter pressing, the clear solution of sodium aurocyanide is run through boxes filled with zinc shavings, when gold deposits as a black slime. The slime is melted with a flux in plumbago crucibles and then refined.

$$2Na[Au(CN)_2]+Zn = 2Au+Na_2Zn(CN)_4.$$

The 'tailings' from amalgamated plates which still contains some gold are also treated by the cyanide process.

(iii) Chlorination process.— The auriferous pyrites are roasted and treated with chlorine—the auric chloride is leached with water and the gold precipitated by ferrous sulphate : $AuCl_3+3FeSO_4 = Au+FeCl_3+Fe_2(SO_4)_3$.

Refining.— Crude gold contains silver, copper and sometimes lead. Lead, if present is eliminated by cupellation. Copper is removed from gold bullion by oxidising fusion with borax and nitre.

Silver and gold are separated by boiling the granulated alloy with concentrated sulphuric acid in a cast iron pot, when silver alone dissolves—the residue of gold is melted and cast into ingots. The process is called *parting.*

For parting the alloy must not contain more than one-third of gold, otherwise silver is not dissolved. When the alloy contains more, it is melted with silver so that it contains one-quarter its weight of gold, and hence the process is called **quartation.** Parting is also carried out with concentrated nitric acid.

Uses of gold.— (i) Gold is used in ornaments and coinage. Pure gold is too soft and is, therefore, alloyed with copper or silver or both, for the above purposes.

The *fineness* of gold is expressed in carats, pure gold being 24 carat, and the five standard alloys are 22, 18, 15, 12 and 9 carat, i.e., parts of gold in 24 of alloy.

(ii) Gold also finds use in *gilding*, i.e., covering a base metal with a thin layer of gold, usually by electrolysis. Gold plating is made by electro-deposition from a bath containing potassium aurocyanide (p. 129).

(iii) Purple of Cassius is used for making ruby glass. *Purple of Cassius* is obtained as a purple powder by precipitating gold chloride with stannous chloride—it consists of hydrated stannic oxide with finely divided (colloidal) gold adsorbed on it. The formation of *purple of Cassius* is utilised as a sensitive test for gold. $2AuCl_3+3SnCl_2+6H_2O = 2Au+3SnO_2+12HCl$.

Properties.— (i) Gold is the most malleable and ductile (and can be beaten into leaves 0·00009 mm. thick—gold leaves transmit green light), rather soft metal with a beautiful yellow lustre and a high sp. gr. of 19·3, and is a good conductor of heat and electricity.

(ii) Gold is a noble metal. It does not tarnish in air. It is unattacked by oxygen or any single acid *except selenic acid* which dissolves gold, nor is it attacked by alkalis—fused alkalis and nitrates or sodium peroxide, however, attack it.

(iii) Gold is attacked by the halogens, and therefore by *aqua regia* which yields chlorine and converts gold into chlorauric acid :

$$2Au + 3Cl_2 + 2HCl = 2H[AuCl_4].$$

Gold slowly dissolves in potassium cyanide solution in presence of air, giving potassium aurocyanide, $K[Au(CN)_2]$.

Gold compounds

Gold forms two series of compounds—*aurous* compounds, all sparingly soluble, in which the gold is *univalent,* and *auric* compounds in which it is tervalent.

Auric chloride, $AuCl_3$.—Gold dissolves in aqua regia to a yellow solution which on concentration yields yellow crystals of hydrated chlorauric acid, $HAuCl_4,4H_2O$. $2Au+3Cl_2+2HCl = 2H[AuCl_4]$.

These lose hydrogen chloride at 120° to form deep red crystals of auric chloride, $AuCl_3$.

The chlorauric acid, commonly called 'gold chloride', is soluble in water, alcohol and ether. Its solution is readily reduced to metal by hydrogen or by exposure to light (and hence its use in photography for toning the prints).

It forms salts, e.g., light yellow crystals of $2K[AuCl_4].H_2O$ on treatment with concentrated HCl and KCl; colourless crystals of potassium auricyanide $K[Au(CN)_4]$ with potassium cyanide.

Aurous chloride, AuCl—It is an insoluble yellow powder formed by heating auric chloride at 175°: $AuCl_3 = AuCl + Cl_2$; at higher temperatures it decomposes into gold and chlorine, but with water it gives gold and auric chloride: $3AuCl = 2Au + AuCl_3$.

Aurous chloride forms potassium aurochloride $K[AuCl_2]$.

Aurous hydroxide, AuOH, is precipitated as a violet powder by the action of cold dilute alkali upon aurous chloride. It is a very weak base. At 200°C it is said to form violet-grey *aurous oxide*, Au_2O (which may be a mixture of gold and auric oxide, Au_2O_3).

Auric hydroxide, $Au(OH)_3$, a reddish-brown powder, is formed by the action of alkali on gold chloride $HAuCl_4$. It is a very weak base. At 150° it forms *auric oxide*, Au_2O_3. Both the oxides are unstable, and yield metallic gold and oxygen on gentle heating.

Fulminating gold, an olive-green powder, is made by digesting auric hydroxide with ammonia. It is formulated as $HN = Au-NH_2, 3/2H_2O$. When dry it detonates violently when heated or struck.

$$Au(OH)_3 + 2NH_3 = HN = Au-NH_2 + 3H_2O.$$

Potassium aurocyanide, $KAu(CN)_2$, is made by dissolving fulminating gold in boiling potassium cyanide solution; it separates as colourless crystals on cooling. Potassium aurocyanide is used in gold plating.

$$KAu(CN)_2 \rightleftharpoons K^+ + Au(CN)'_2;\quad Au(CN)'_2 \rightleftharpoons Au^+ + 2CN'$$

Exercises

1. Give the names and compositions of the chief ores of copper, and explain the chemistry of the extraction of the metal from its sulphide ore. Write equations, stating conditions, for the actions of nitric and sulphuric acids upon metallic copper. Mention the uses of the metal and its alloys. Starting from copper how you would prepare a sample of cuprous chloride?
Madras '49.

2. How is blue vitriol produced from scrap copper? How would you obtain pure copper sulphate from blue vitriol containing traces of ferrous sulphate? Starting with copper sulphate, how may (a) metallic copper, (b) cuprous oxide, (c) cuprous chloride, (d) cupric chloride, be prepared?
Calcutta '46.

3. Explain the changes that take place when a solution of copper sulphate is treated with (a) sodium chloride solution in presence of sulphur dioxide, (b) scrap iron, (c) potassium iodide, (d) caustic soda solution in presence of a reducing agent, (e) ammonia. *Cambridge 1st M.B.*

4. Mention the principal sources of silver. Describe a method for the extraction of silver from argentiferous lead. How is the metal obtained in a pure condition? How can a coating of silver be applied on the surface of a metal and glass? *U. P. Board* '42.

5. Explain what happens when: (a) ammonium hydroxide is added to silver nitrate solution, (b) silver glance is treated with sodium cyanide solution, (c) copper scrap is treated with dilute sulphuric acid in a current of air, (d) air is blown over the surface of molten argentiferous lead, (e) a mixture of copper filings and black oxide of copper is boiled with stong hydrochloric acid, (f) silver chloride is treated with metallic aluminium in dilute sulphuric acid.

6. Write notes on recovery of gold from an alloy of gold and silver.
Bombay '53.

7. What happens when a solution of silver nitrate is treated with (a) caustic soda, (b) potassium cyanide, (c) ammonium hydroxide? How are pure silver and silver nitrate made from a silver coin containing Ag and Cu?
Madras '49.

8. Write notes on photography, cupellation and desilverisation of lead.

XXXIII

Iron, cobalt and nickel

The triad of transitional elements (p. 163) Fe, Co, and Ni belongs to eighth group in the periodic table.

	At. no.	At. wt.	Density	At. vol.	M. pt. °C	B. pt. °C
Iron	26	55·85	7·86	7·1	1539°	2450°
Cobalt	27	58·94	8·8	6·7	1478°	2900°
Nickel	28	58·69	8·8	6·7	1452°	2900°

The metals usually occur together in nature. They are hard, greyish-white metals with high densities and high m.ps, and low atomic volumes. They are *magnetic* and possess catalytic properties. They occlude hydrogen. *Iron rusts in air*, but Co and Ni do not and hence their use to protect iron from rusting.

They show *variable valency* and form *coloured ions*—the colour of *bivalent ions* of Fe, Co and Ni are pale green, red and green respectively, and the colour of *trivalent ions* of Fe and Co are *yellow* and *blue* respectively. Ferrous salts are not very stable and gradually pass into stable ferric state. Cobaltous salts are stable whereas the cobaltic salts are very unstable. Nickelous salts are very stable—nickel is exclusively bivalent and forms no nickelic salts.

Iron

History.—Because of its manifold applications, iron is by far the most important metal. It came into general use at a very early date in human history, and gradually displaced bronze, which was in use as early as 3000 B.C. The famous iron pillar at Delhi, remarkable for its freedom from rust, which was probably built about 300 A.D., bears testimony to the fact that iron smelting reached a high level of perfection in ancient India.

Occurrence.—Native iron is rarely found, except in meteorites—the most notable deposit being at Disco Island, Greenland. The most important ores of iron are: **red hæmatite,** Fe_2O_3; **brown hæmatite** or *limonite*, $2Fe_2O_3, 3H_2O$; **magnetite,** Fe_3O_4; and *spathose* or **spathic iron ore** or *siderite*, $FeCO_3$. *Iron pyrites*, FeS_2 is important as a source of sulphur—burnt pyrites, chiefly ferric oxide, may be smelted for iron.

Huge deposits of iron ores, chiefly hæmatite, are found in Maurbhunja, Keonjhur, Singhbhum, Mysore, and elsewhere in India. Principal iron producing centres in India are Jamshedpur in Bihar, Kulti and Burnpur in West Bengal, and Bhadrabati in Mysore. Huge iron smelting projects have recently been started at Rourkella (Orissa), Vilai (M.P.) and Durgapur (West Bengal). The Indian hæmatite ores contain 60 to 65 per cent of iron on an average.

Metallurgy.—The iron ores which contain much sulphur, phosphorus and arsenic are not suitable as sources of the metal as these impurities would render it brittle and unworkable. Iron is extracted from its oxide and carbonate ores only (burnt pyrites which is chiefly ferric oxide, is sometimes used) by reduction with carbon in a blast furnace. The process is carried out in two steps:

(i) Preliminary roasting or calcination.— The ore is burnt with a little coal in heaps or in shallow kilns in order to drive off most of the moisture, carbon dioxide, sulphur and arsenic; ferrous oxide is converted to ferric oxide to avoid the formation of ferrous silicate in the slag during smelting. The ore is also rendered porous. The roasted mass contains ferrix oxide, Fe_2O_3.

Smelting or reduction in the blast furnace.— The roasted ore is mixed with coke and *limestone* (flux) and charged into the blast furnace (fig. 189), where the ferric oxide is reduced to iron.

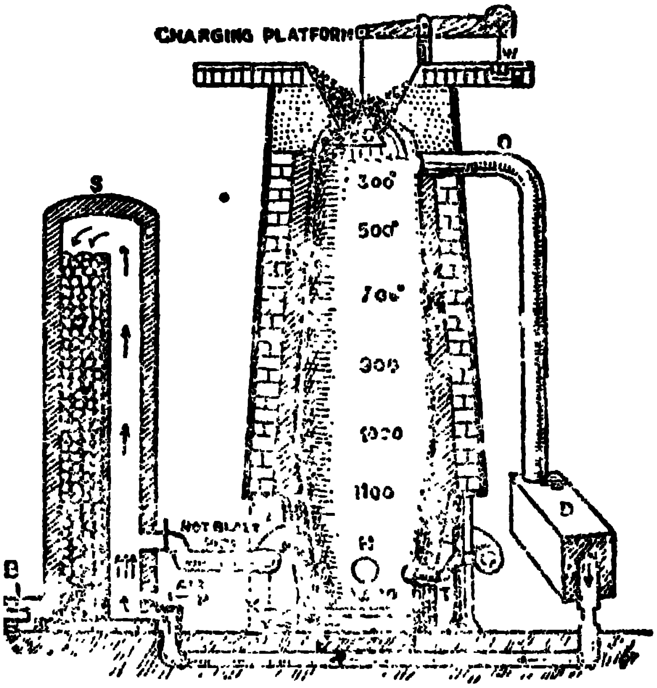


Fig. 189

The blast furnace is a cylindrical, vertically placed shaft made of steel plates lined internally with refractory firebricks, and about 50—100 ft. in height and 15-20 ft. in diameter. The furnace broadens slightly from the top downwards, reaching the broadest point (about two-thirds of the way to the ground) at the *boshes*, and then narrows gradually to a **hearth** (about 10 ft. in diameter and the same height) at the base. The hearth is provided with two plug holes, stopped with clay, for letting out the molten slag and iron respectively, the *slag hole* is at a rather higher level than the tapping hole for iron. A little above these plugs the hearth is pierced with a set of holes through which are inserted the nozzles of water-jacketted iron blowing pipes, called **tuyeres.** The mouth is closed with **a cup and cone device** meant for introducing the charge into the furnace.

The furnace is started by burning piles of wood inside, and a mixture of roasted ore, hard coke, and limestone is intermittently fed into the furnace by means of the cup and cone device—the charge consists of 1 ton of coke and 10 cwt. of limestone to 2½ tons of ore, which produce 1 ton of cast iron. A blast of dry (by passing over silica gel) air, preheated to about 800°C, is forced into the base of the furnace through the *tuyeres.* The coke burns in the air blast to carbon monoxide and raises the temperature to about 1500°C. $2C + O_2 = 2CO$. The temperature of the furnace increases continually from the mouth (400°) to the hearth (1500°).

The descending charge of solids meets the current of hot carbon monoxide passing upwards when the following reactions take place, leading to the formation of iron.

Above the boshes at about 600°—900°, the ferric oxide is reduced by carbon monoxide to spongy iron. $Fe_2O_3 + 3CO \rightleftharpoons 2Fe + 3CO_2$.

But the reaction being *reversible*, the reduction is not complete at this stage. The spongy iron absorbs sulphur from the fuel. The limestone in the charge is decomposed into lime and carbon dioxide.

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

Near the centre of the furnace at about 900°, the reaction: $2CO \rightleftharpoons CO_2 + C$ deposits finely divided carbon which completes the reduction $Fe_2O_3 + 3C \rightleftharpoons 2Fe + 3CO$. The phosphates and the manganese compounds in the ore, and also a part of silica are reduced to phosphorus, manganese and silicon which readily alloy with iron.

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C = 3CaSiO_3 + 2P + 5CO.$$

$$SiO_2 + 2C = Si + 2CO; \quad Mn_2O_3 + 3C = 2Mn + 3CO$$

The remainder of the silica (the gangue in the ore) combines with lime to form a fusible *slag of calcium silicate*: $CaO + SiO_2 = CaSiO_3$.

At the hearth of the furnace at about 1500°, the iron containing carbon, sulphur, phosphorus, manganese, and silicon, fuses—the slag floats on the surface of molten iron and thereby prevents its oxidation by the air blast. The molten slag runs out from above the molten iron. The molten iron is tapped out at intervals into sand moulds to form **pig iron** (or cast iron), or is sent in the molten state to steel furnaces. The molten iron is directly cast into V-shaped bars called *pigs*. **Cast iron** is re-melted pig iron.

The hot exhaust gases, leaving the furnace by an outlet at the top, and having the composition—nitrogen 60, CO 24, CO_2 12, CH_4 and H_2 4 by volume are utilised in preheating the air blast in Cowper's stoves on a regenerative principle. The blast furnace operates day and night for years until its lining wears out.

The slag finds applications in the reclamation of land; for road making; in the manufacture of 'slag wool' and cement.

Varieties of iron.— Three varieties of commercial iron are *cast iron, wrought iron* and *steel.*

Cast iron (pig iron).— It contains 2·2 to 4·5 per cent of carbon, together with silicon (0·5 to 2 per cent.), manganese (0·2 to 1 per cent.), phosphorus (0·7 per cent.), and sulphur (0·3 to 1 per cent.) in small amounts. Carbon may be present in the free state as *graphite* or in combination as iron carbide, Fe_3C (cementite). *White cast iron,* containing *cementite* is obtained on *rapidly* cooling the molten iron, while on *slow* cooling carbon separates as graphite giving a product called *grey cast iron.* Cast iron melts at 1200°, and is very hard and brittle, and hence is of little value for structural purposes.

It finds uses in making castings which are not subjected to violent shocks e.g., fire grates, lamp-posts, railings, pipes, parts of machinery, etc. About three quarters of the total output of cast iron is made into steel and a small quantity into wrought iron.

Wrought iron.— *Malleable* or *wrought* iron is very nearly pure iron, containing only 0·12 to 0·25 per cent of carbon, and melts at a higher temperature (1400° to 1500°) than cast iron.

It is made by oxidising away the carbon and other impurities in cast iron by melting the latter on the bed of a reverberatory furnace, lined with hæmatite, Fe_2O_3. In order to bring the iron into intimate contact with the lining, the molten mass is stirred or *puddled* with a rabble, and hence the operation is called **puddling process.** The hæmatite oxidises the carbon: $Fe_2O_3 + 3C = Fe + 3CO$, the carbon monoxide bubbling through the molten iron causes the latter to swell up and appear to boil. Silicon, manganese, and phosphorus, etc., are oxidised and pass into the slag. As the impurities are removed from the iron, its melting point rises, and it becomes pasty. It is then formed into balls or "blooms" which are beaten with steam hammers to squeeze out the slag, and then forged into bars. Wrought iron containing phosphorus is brittle at ordinary temperature and is called *cold-short*; sulphur makes the iron brittle at red heat, and is said to be *red-short*.

Soft and malleable, it can be easily welded and worked by hammering, and hence its use by the blacksmiths. Fibrous in structure, it has a high tensile strength. It finds uses in making chains, wire anchors, and cores of electromagnets.

Steel. Steel is an alloy of iron with a carbon content of 0·15 (mild steel) to 1·5 per cent (hard steel). It may be made (i) from cast iron, (ii) from wrought iron.

Steel from cast iron.—Steel is produced from cast iron by first *removing the impurities* in cast iron, e.g., C, Si, Mn, S, and P, by oxidation, and then adding the correct *amount of carbon* according to the quality of steel desired.

The operation is carried out by Bessemer process or the *Siemens-Martin* open-hearth process. There are two modifications of each process (i) **the acid process** for the treatment of cast iron which is free from phosphorus—the converter or the hearth is lined with *silica bricks* in the acid process; (i) **the basic process** for the treatment of cast iron containing phosphorus—in the basic process the converter or the hearth is given a lining with *calcined dolomite* or *magnesite.* Iron containing phosphorus cannot be treated by the acid process, *since an interaction between the phosphatic slag and silica lining would occur.*

The Bessemer process (1855).—The process is carried out in a converter (fig. 190) which is a large pear-shaped iron vessel (holding 10 tons of metal) with a perforated bottom through which a blast of air can be forced in fine jets. It is supported on two horizontal arms (trunnions) so that it can be tilted in a vertical plane. The converter is lined with refractory silica bricks (*acid lining*) or with magnesia and lime (*basic lining.*)

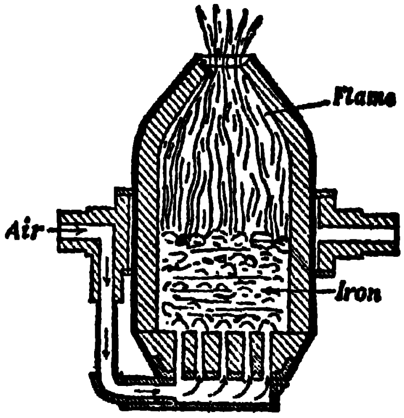


Fig. 190

The acid Bessemer process is used to treat cast iron free from phosphorus. The converter is tilted in a horizontal position and the charge of molten cast iron is run in through the mouth. The blast of air is then turned on, and the converter is swung into the vertical position.

Air rises through the molten metal in small bubbles and rapidly brings about the oxidation of the impurities—the heat of oxidation keeps the metal in the molten state. Silicon and manganese are first oxidised and pass into the *slag* as manganese silicate. $2Mn+O_2 = 2MnO$; $Si+O_2 = SiO_2$; $MnO+SiO_2 = MnSiO_3$. Carbon is then oxidised to carbon monoxide which *burns* at the mouth of the converter with an *orange-yellow flame* edged with blue. After 6 to 8 minutes the flame drops indicating that the carbon has been removed.

$$2C+O_2 = 2CO; \quad 2CO+O_2 = 2CO_2.$$

The converter is again tilted, the blast stopped, and a charge of requisite amount of **spiegeleisen** (an alloy of iron, mangamese and carbon) added to the molten iron for *deoxidation* and *recarburisation*—the blast is continued just for a few moments to bring about a thorough mixing. C and Mn act as *deoxidisers* in the first instance and reduce any oxide of iron that is present—the excess dissolves in the molten iron to form steel. The molten steel is then poured into ladles by tilting the converter, separated from the slag floating on the top, and run into moulds.

Sometimes *a little Al* or *ferro-silicon* is added to molten steel to avoid blow holes in the castings due to bubbles of gas which react with the added elements.

The basic Bessemer or the Thomas-Gilchrist process used to treat cast iron containing phosphorus. A charge of *limestone* and coke is first introduced into the converter and the blast of air turned on. The molten cast iron is then run in and the blast continued.

Silicon and manganese are at first oxidised and pass into the slag; then carbon and phosphorus are oxidised simultaneously; carbon monoxide burns at the mouth of the converter. The air blast is continued after the carbon monoxide flame sinks for the completion of the oxidation of phosphorus. The phosphorus pentoxide reacts with lime and forms a slag containing calcium phosphate and free lime (basic slag). $4P+5O_2 = 2P_2O_5$; $4CaO+P_2O_5 = Ca_3(PO_4)_2,CaO$.

The molten iron is poured out into a ladle, *separated from the slag*, (the basic slag must be removed before spiegeleisen is added, as otherwise the phosphorus would again pass back into iron), and *then* mixed with a charge of requisite amount of *spiegeleisen* for *recarburisation* and *deoxidation*, to form the steel. The basic Bessemer slag, also called **Thomas slag**, contains calcium phosphate and is used as a fertiliser.

Analysis of a sample of cast iron and steel made from it is given below:

	Fe	C	Si	Mn	P	S
Steel	99·4	0·18	0·003	0·36	0·02	0·037
Cast iron	93·5	1·8	1·4	1·7	1·5	0·10

The open hearth process (1863-64).—Most of the high grade steels are now made by the open-hearth furnace (fig. 191). Molten cast iron is run on the hearth which is lined with silica in the acid process (if the iron is free from phosphorus) or with lime and magnesia in the basic process (if phosphorus is present). *Scrap steel and oxide ore* of iron (hæmatite) are added to the charge of cast iron—limestone is also added if the iron contains phosphorus. The charge is melted by heating the furnace regeneratively with producer gas—the air and producer gas

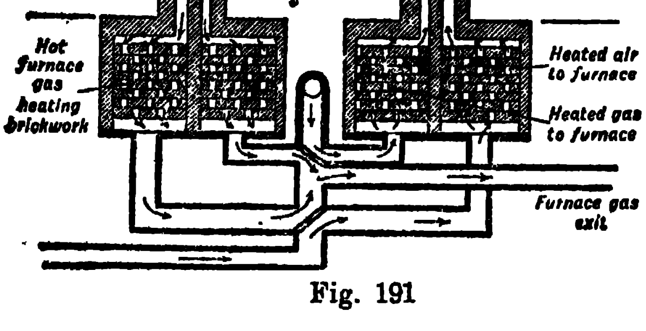


Fig. 191

are injected through separate regenerators of chequer brick work used in pairs and alternately crossed by the hot exhaust gases and the fuel gases.

Silicon, manganese, and a greater part of the carbon are oxidised by the iron oxide—the oxides of silicon and manganese producing a slag of manganese silicate and carbon monoxide bubbling through the molten air. The remaining carbon and phosphorus are oxidised by the excess of air admitted to the furnace —the oxide of phosphorus forming a slag of calcium phosphate, as in Bessemer process.

The molten iron is then poured out into ladles, separated, from the slag and a charge of *spiegeleisen* is added, after the removal of the slag, for reoxidation and recarburisation. A little Al or ferro-silicon is added to finished steel to avoid blow holes in castings.

The open hearth process offers several advantages over the Bessemer process : (i) The composition of the product can be accurately followed and controlled, all the impurities including phosphorus being *completely* eliminated, and hence high grade steels are produced. Phosphorus is only *incompletely* removed by the Bessemer process, (ii) Scrap iron and oxide ore can be utilised; the open hearth process calls for a good deal of steel scrap. (iii) Cast iron from low grade ores can be used.

The open hearth operation lasts 8-10 *hours* and requires the use of fuel gases, whereas the Bessemer process is complete within 8-10 minutes and needs no fuel. About 80% of the total output of steel is made by the open hearth process.

A combination of the acid Bessemer and the basic open hearth is often practised for the treatment of phosphatic pig iron, and is known as the Duplex **process.** Electric furnaces are used for making special high quality steel by refining the Bessemer or open hearth steel.

Steel from wrought iron.— In the **cementation process** bars of wrought iron are embedded in powdered charcoal in fire brick boxes set in a furnace, and heated at 1000° for about two weeks—hot gases from a grate heat the boxes on the outside. Carbon is gradually absorbed, and the wrought iron is converted, *without fusion*, into a product, called *blister steel* owing to its appearance. This may be converted into **shear steel** (used for cutlery) by forging under a steam hammer or into **crucible steel** (used for high-grade tools) by fusion in graphite crucibles. Wrought iron is case-hardened by heating in contact with carbon, when a surface layer of hard steel is formed. *Armour plate* is made by case-hardening soft steel. An extremely hard surface, used for cylinder bores, etc., is formed by **nitriding** *i.e.*, by heating aluminium steel (containing 1 per cent aluminium) in an atmosphere of ammonia at about 450° to 500°C.

Properties of steel.—The properties of steel depend on the content of carbon and on the heat treatment to which it has been submitted. Low carbon steels are soft like wrought iron and are called *mild steel* (0·1 to 0·5% of carbon). Low and medium carbon steels are malleable and can be welded and forged like wrought iron. Steel has a high tensile strength. The hardness and tensile strength increase, and the malleability decreases, with increasing carbon content.

The hardness of steel can be modified by proper heat treatment. On being heated to redness and then plunged into cold water it becomes extremely hard **(hardening of steel).** The hardened steel may be softened to any desired extent by **tempering,** i.e., heating it to a *selected* temperature between 230° to 300° and then allowing it to cool slowly. *The tempered steel* possesses the hardness and toughness required in razor blades, chisels, saws and springs.

Modern machine civilisation depends largely upon the numerous applications of iron and steel. Steel, for example, is used in making machine tools, implements of war and agriculture, rail lines, locomotives, cutlery, and magnets, etc.

Alloy steels.—Steels containing other metals alloyed with iron are known as alloy steels. The metals extensively used in alloy steels are Cr, Mn, Ni, V, W, Mo and Si. The alloying metals, usually added as ferro alloys, e.g., ferrochrome and ferromanganese, to the molten iron during recarburisation, imparts special properties on steel. The alloy steels are generally made in electric furnaces. Few alloy steels are:

Name	Alloying metal	Properties	Uses.
Nickel steel	3·25% Ni; 0·2—0·5%C	High elasticity and ductility.	Structural purposes.
Invar	35 per cent nickel	Low coefficient of expansion	Pendulum rod; metre scale.
Platinite	46 per cent nickel	Same coefficient of expansion as glass	Glass to metal seals; electric lamp bulbs.
Manganese-steel	12—13% Mn; 0·9-2%C	Very hard; resistant to wear	Jaws of rock crushers.
Chrome steel	0·5—2 per cent Cr.	Very hard; high tensile strength	Ball bearings; dies; files.
Chrome-nickel steel	4% Ni; 2% Cr; 0·33%C	High elasticity & tensile strength	Armour plates; motor cars.
Stainless steel	10—15% Cr; 0·3%C	Resists corrosion; rustless iron	Stainless cutlery; valves; turbine parts.
Chrome-vanadium steel	0·7—1·4% Cr; 0·4—0·25 per cent vanadium	High tensile strength; resistance to stresses.	Automobile axles and springs.
High speed tool steel	18% tungsten; 5% Cr; 0·3% V; 0·7% C.	Retains temper & hardness at red-heat	High speed lathe tools.
Duriron, tant iron, ironac	About 16% Si	Resistant to acid corrosion	Acid-resisting vessels.
Allegheny	17-20% Cr; 7-10% Ni; 0·5% O; 0·5% Mn.	High resistance to corrosion.	

Mischmetal (mixed metal) is an alloy of iron with about 70% cerium and smaller amounts of other rare earth metals (such as lanthanum); when sparked it gives hot sparks which will kindle petrol vapour or coal gas, and hence its use in automatic gas and cigarette lighters.

Comparison of different varieties of iron.— The properties of iron depend largely upon the content of carbon. The properties of cast iron, steel and wrought iron are as follows:

Properties	*Cast iron*	*Steel*	*Wrought iron*
(i) *Amount of carbon*	2·2—4·5%	0·15 to 1·5%	0·12 to 0·25%
(ii) *Melting point*	1200°C	1300°—1400°C	1500°C
(iii) *Hardness*	Hard	Hard and soft	Soft
(iv) *Brittleness/malleability*	Brittle	Malleable/brittle	Malleable
(v) *Tempering*	Cannot be tempered	Can be tempered	Cannot be tempered.
(vi) *Welding*	Cannot be welded	Can be welded	Can be welded
(vii) *Magnetisation*	Cannot be permanently magnetised	Can be permanently magnetised	Cannot be permanently magnetised.

The Rusting of iron.— On exposure to ordinary moist air commercial iron becomes covered with a reddish-brown deposit of hydrated ferric oxide, mainly

$2Fe_2O_3.3H_2O$, known as *rust*. *An impurity in the iron is necessary to cause rusting—pure iron does not rust.* It has been shown that the initial step in rusting is an electrolytic process—different parts of a specimen of iron act as poles of voltaic cells, the impurities setting up centres of rusting. At the anode iron passes into solution as ferrous irons, Fe^{++}, while at the cathode hydrogen ions (from the water: $H_2O \rightleftharpoons H^+ + OH^-$) are discharged.

Iron dissolves *At cathode* $2H^+ + 2e = H_2$
At anode $Fe—2e = Fe^{++}$ *Hydrogen liberated.*

For rusting to occur, the presence of liquid water and oxygen are essential; the water supplies the hydrogen ions, while the oxygen acts as a depolariser in oxidising the nascent hydrogen at the cathode to water.

The ferrous ions, Fe^{++}, which pass into solution as the initial step in rusting and the hydroxyl ions, OH^- (from water), combine to form ferrous hydroxide, which is then oxidised by the air and deposited as hydrated ferric oxide.

$$Fe + 2H^+ = Fe^{++} + H_2; \quad Fe^{++} + 2OH^- = Fe(OH)_2$$
$$2Fe(OH)_2 + O = Fe_2O_3,H_2O + H_2O$$

Rusting is greatly accelerated by carbon dioxide (since carbonic acid furnishes the H^+ ions) and metallic salts such as dissolved chlorides in the water, but it is retarded by alkalis. Hence the factors which influence rusting in moist air are: (i) the purity of the iron and the nature of its surface, (ii) the presence of dissolved substances in the water. Metals such as chromium and nickel which form solid solution with steel render it rustless.

Iron is usually protected from rusting by metallic coatings, e.g. tinning, galvanisation, nickel-plating, chromium-plating, etc. and by coatings of paints, varnishes, lacquers, enamels, coal tar, asphalt etc.

Properties of iron. (i) Pure iron is a soft white metal which is highly tenacious, malleable and ductile. It is *magnetic.*

Pure iron may be obtained by electrolysis of an aqueous solution of ferrous chloride at 110° or by reducing ferric oxide in hydrogen at 1000°—*reduced iron* is pyrophoric.

(ii) Stable in dry air, it *rusts* in moist air. It burns brilliantly in oxygen when heated to redness, throwing off sparks of Fe_3O_4.

(iii) It is oxidised at a red heat by air or steam to ferroso-ferric oxide, Fe_3O_4: $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$.

(iv) It dissolves readily in dilute hydrochloric or sulphuric acid to give hydrogen and a *pale green ferrous salt*: $H_2SO_4 + Fe = FeSO_4 + H_2$. Iron also dissolves in dilute or fairly strong nitric acid (p. 250).

Passive iron.—Iron is rendered *passive* by immersion in concentrated nitric acid. The passive iron is insoluble in dilute acids and does not precipitate copper from a solution of copper sulphate. The passivity is due to the formation of a thin continuous film of Fe_2O_3 on the surface of iron; passivity is removed by scratching the metal or by touching it with a piece of active iron under dilute sulphuric acid, or by heating it in hydrogen.

Iron also becomes passive in solutions of oxidising acids, e.g., chromic, chloric and iodic acids, and by anodic oxidation.

(v) It precipitates copper from a solution of cupper sulphate:

$$CuSO_4 + Fe = Cu + FeSO_4.$$

(vi) It combines directly, when heated, with carbon, sulphur, chlorine, yielding the *carbide*, Fe_3C, the ferrous sulphide, FeS, and the ferric chloride, $FeCl_3$, respectively. *Iron is not attacked by alkalis.*

Compounds of Iron

Iron forms two series of compounds, e.g., *ferrous compounds* in which the metal is *divalent*, and *ferric compounds* in which the metal is *trivalent*. Ferrous salts gradually pass into the ferric state on exposure to air.

Ferrous salts are nearly colourless in solution, but usually possesses a *green* tinge. Ferric irons are almost colourless, but undissociated ferric chloride is yellow in colour.

Ferrous salts are readily oxidised to the ferric state: (i) by atmospheric oxygen, especially in presence of an acid or hydrogen peroxide.

$$4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O$$

(ii) by chlorine or bromine, $2FeCl_2 + Cl_2 = 2FeCl_3$.

(iii) by boiling with aqua regia or nitric acid,

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

Ferric salts are reduced to the ferrous state:

(i) by nascent hydrogen in acid solution, e.g., zinc and hydrochloric acid,

$$FeCl_3 + H = FeCl_2 + HCl,$$

(ii) by hydrogen sulphide or sulphur dioxide,

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S,$$

$$2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + H_2SO_4 + 2HCl,$$

(iii) by stannous chloride, $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$.

Oxides of iron.—(i) Ferrous oxide, FeO, is obtained as a pyrophoric black powder by reducing ferric oxide with hydrogen at 300° or by heating ferrous oxalate in absence of air $FeC_2O_4 = FeO + CO + CO_2$.

(i) Ferric oxide, Fe_2O_3, is prepared by igniting ferric hydroxide or ferrous sulphate in air. $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$. The product obtained from the sulphate is a red powder and is used under the name of **rouge** as a pigment in cosmetics and as a polishing powder. Ferric oxide is used as a pigment under the names *Venetian red*, *Indian red* and *red ochre*. Ferric oxide occurs naturally as *haematite* and *limonite*.

Insoluble in water, it dissolves in acids to form ferric salts, but the ignited oxide is only sparingly soluble. It is a basic oxide, but it exhibits feebly acidic properties in forming ferrites, e.g., sodium ferrite, $NaFeO_2$.

$$Na_2CO_3 + Fe_2O_3 = 2NaFeO_2 + CO_2.$$

(iii) Ferroso-ferric oxide, magnetic oxide of iron, Fe_3O_4, is formed by heating iron to redness in air or steam (p. 184).

It is a black strongly magnetic substance, insoluble in water but soluble in acids to form ferrous and ferric salts, and hence it appears to be a mixed oxide of ferrous and ferric oxides, $FeO.Fe_2O_3$. Very resistant to the attack of chlorine or oxygen, it is used as an electrode in electrolysis, and in arc lights.

Ferrous hydroxide, $Fe(OH)_2$. is obtained as a white precipitate by adding caustic soda to the solution of a ferrous salt, with absolute exclusion of air: $FeSO_4 + 2NaOH = Na_2SO_4 + Fe(OH)_2$.

But on exposure to the air it turns green and then brown as it is oxidised to ferric hydroxide.

Unlike ferric hydroxide, ferrous hydroxide is not completely precipitated from the solution of a ferrous salt by the addition of ammonia and ammonium chloride. and hence the solution of group IIIA in qualitative analysis is boiled with nitric acid to oxidise to the ferric state any ferrous iron that may be present.

Ferric hydroxide, $Fe(OH)_3$, obtained as a reddish-brown precipitate by the addition of ammonia, caustic soda, or sodium carbonate to the solution of a ferric salt.

$$2FeCl_3 + 3Na_2CO_3 + 3H_2O = 2Fe(OH)_3 + 6NaCl + 3CO_2.$$

It differs from aluminium hydroxide in being insoluble in excess of alkali. Hydrated ferric oxide is used in purification of coal gas.

Ferrous carbonate, $FeCO_3$, is thrown down as a white precipitate on the addition of sodium carbonate to the solution of a ferrous salt, with absolute exclusion of air. It turns green and finally brown on exposure to air, owning to oxidation to ferric hydroxide. It dissolves in water containing carbon dioxide, forming ferrous bicarbonate, $Fe(HCO_3)_2$, which is readily oxidised to ferric hydroxide on exposure to air :

$$4Fe(HCO_3)_2 + 2H_2O + O_2 = 4Fe(OH)_3 + 8CO_2.$$

Ferric carbonate is not known. Ferric hydroxide is precipitated on the addition of sodium carbonate to the solution of ferric salt, *vide supra.*

Ferrous chloride, $FeCl_2$, is formed anhydrous, in colourless crystals, on heating iron in a current of dry hydrogen chloride or by heating ferric chloride in hydrogen:

$$2HCl + Fe = FeCl_2 + H_2 ;\quad 2FeCl_3 + H_2 = 2FeCl_2 + 2HCl.$$

The pale green monoclinic crystals of the hydrate, $FeCl_2,4H_2O$, deposit on evaporating a solution of iron in hydrochloric acid.

Ferric chloride, $FeCl_3$, is obtained in the anhydrous state by passing chlorine over red-hot iron. $2Fe + 3Cl_2 = 2FeCl_3$. It is deposited in black scales, m. p. 300°, which rapidly vaporise on heating; its vapour density at 444° corresponds to the formula Fe_2Cl_6. But at higher temperatures dissociation occurs:

$$Fe_2Cl_6 \rightleftharpoons 2FeCl_3 \rightleftharpoons 2FeCl_2 + Cl_2.$$

It dissolves readily in water—the solution is *acidic* due to hydrolysis. $FeCl_3 + 3HOH \rightleftharpoons 3HCl + Fe(OH)_3$. It is also soluble in alcohol, ether and benzene.

It is obtained in solution by dissolving ferric hydroxide in hydrochloric acid or by saturating a solution of ferrous chloride with chlorine. The solution on evaporation deposits yellow crystals of the hydrate, $FeCl_3,6H_2O$. $2FeCl_2 + Cl_2 = 2FeCl_3$. Ferric chloride readily libertes iodine from potassium iodide solution:

$$2FeCl_3 + 2KI \rightleftharpoons 2FeCl_2 + 2KCl + I_2.$$

It is used as a styptic, i.e., in stopping blood, in medicine, and as a reagent in the laboratory.

Ferrous nitrate, $Fe(NO_3)_2$, is best obtained by treating a solution of ferrous sulphate with barium nitrate : $FeSO_4 + Ba(NO_3)_2 = BaSO_4 + Fe(NO_3)_2$, since it is difficult to prevent oxidation of the ferrous salt when iron is dissolved in dilute nitric acid. On evaporating at a low temperature, green crystals of the hexahydrate, $Fe(NO_3)_2$, $6H_2O$, deposit, which are very soluble in water, but readily pass into the ferric state.

Ferric nitrate, $Fe(NO_3)_3$, is obtained by dissolving iron in hot dilute nitric acid—colourless crystals of $Fe(NO_3)_3$, $9H_2O$ separate. It dissolves in water giving a *brown* solution, which becomes colourless on the addition of concentrated nitric acid. It finds use as a mordant in dyeing.

Ferrous sulphate, green vitriol or copperas, $FeSO_4,7H_2O$, is prepared in the laboratory by dissolving iron in dilute sulphuric acid and evaporating to crystallisation; $Fe+H_2SO_4 = FeSO_4+H_2$, when pale green monoclinic crystals of the heptahydrate deposit.

It is obtained as a by-product from the waste liquor of H_2S-Kipp (which is charged with ferrous sulphide and dilute H_2SO_4 : $FeS+H_2SO_4 = H_2S+FeSO_4$, by filtering and crystallising the solution.

It is prepared *commercially* by the slow oxidation of *marcasite*, FeS_2, (*iron pyrites is stable in air, unless it is first roasted*) by moist air, when ferrous sulphate and sulphuric acid result:

$$2FeS_2+7O_2+2H_2O = 2FeSO_4+2H_2SO_4.$$

Marcasite is stacked in heaps and exposed to air and water for several days, and then leached with water—the resulting solution is neutralised by scrap iron: $Fe+H_2SO_4 = FeSO_4+H_2$ (ferric iron if any is reduced to the ferrous state by the nascent hydrogen), and evaporated to crystallisation.

Properties. (i) It forms *pale green* efflorescent crystals of the heptahydrate, $FeSO_4,7H_2O$, isomorphous with the Epsom salt, $MgSO_4,7H_2O$, whilst the less stable penhydrate, $FeSO_4 5H_2O$, is isomorphous with blue vitriol, $CuSO_4,5H_2O$. It readily turns brown on exposure to air, owing to oxidation to ferric sulphate.

(ii) When heated the crystals lose their water of crystallisation, leaving the white amorphous anhydrous salt, which decomposes at a red heat, yielding ferric oxide, called *rouge*.

$$2FeSO_4 = Fe_2O_3+SO_2+SO_3.$$

(iii) It is soluble in water—the solution is *acid* due to *hydrolysis*:

$$FeSO_4+2HOH \rightleftharpoons Fe(OH)_2+H_2SO_4.$$

The solution readily passes into the ferric state by atmospheric oxidation: $4FeSO_4+2H_2SO_4+O_2 = 2Fe_2(SO_4)_3+2H_2O$.

The ferrous sulphate solution absorbs nitric oxide, yielding a brown nitroso-compound, $FeSO_4.NO$. $FeSO_4+NO \rightleftharpoons [Fe.NO]SO_4$.

(iv) Crystals of *ferrous ammonium sulphate* or **Mohr's salt,** $(NH_4)_2SO_4$, $FeSO_4,6H_2O$, deposit on cooling a hot saturated solution containing equimolecular proportions of ferrous sulphate and ammonium sulphate. Mohr's salt is stable in air and is less readily oxidised on exposure to air than ferrous sulphate, and hence its use in volumetric analysis in preference to the latter salt.

Ferrous sulphate is used in the preparation of writing ink and *rouge*; as a mordant in dyeing, and as a weed-killer in agriculture; as a reducing agent.

Ferric sulphate, $Fe_2(SO_4)_3$, is prepared by heating ferrous sulphate with concentrated sulphuric acid:

$$2FeSO_4+2H_2SO_4 = Fe_2(SO_4)_3+SO_2+2H_2O.$$

When heated strongly it decomposes thus:

$Fe_2(SO_4)_3 = Fe_2O_3+3SO_3$. It forms violet octahedral crystals of ferrialum, e.g., $(NH_4)_2SO_4,Fe_2(SO_4)_3,24H_2O$, which are readily soluble in water but are not appreciably hydrolysed.

Ferrous sulphate, FeS, is obtained as a black mass by heating iron with sulphur: $Fe+S = FeS$. Commercial ferrous sulphide contains free iron.

It is formed as a black precipitate by passing H_2S through ferrous sulphate solution containing sodium acetate or by adding ammonium sulphide to a ferrous salt. It dissolves in dilute acids, yielding H_2S; $FeS + 2HCl = FeCl_2 + H_2S$.

Iron disulphide, FeS_2, occurs as *marcasite and iron pyrites.*

Detection of iron.—Dry tests: (i) An iron compound, mixed with sodium carbonate and heated on charcoal in the reducing flame, yields a black mass of iron which is attracted by a magnet.

(ii) When an iron compound is heated in a borax bead, the bead becomes *yellow* in the oxidising flame and *bottle green in the reducing flame.*

Wet tests.— Distinctive reaction of ferrous and ferric iron; used ferrous sulphate and ferric chloride solution.

Reagents: solutions of:	*Ferrous salt*	*Ferric salt*
1. NH_4OH or NaOH	Green precipitate of ferrous hydroxide	Reddish-brown precipitate of $Fe(OH)_3$.
2. Potassium ferricyanide, $K_3Fe(CN)_6$	Deep blue precipitate (Turnbull's blue)	No precipitate but a brown solution.
3. Potassium ferro-cyanide, $K_4Fe(CN)_6$	White precipitate rapidly turning blue	Deep blue precipitate (Prussian blue)*
4. Ammonium thio-cyanate, NH_4CNS	No colouration	Blood-red colouration**

* The Prussian blue is ferric ferrocyanide, $Fe_4[Fe(CN_6]_3$.

$$4FeCl_3 + 3K_4[Fe(CN)_6] = Fe_4[Fe(CN)_6]_3 + 12KCl.$$

** The deep red colouration is due to the ferrithiocyanate ion, $[Fe(CNS)_6]'''$.

$$2FeCl_3 + 6NH_4CNS \rightleftharpoons Fe[Fe(CNS)_6] + 6NH_4Cl.$$

The ferrocyanides.— Potassium ferrocyanide, $K_4Fe(CN)_6$, and potassium ferricyanide, $K_3Fe(CN)_6$, contain the stable complex ferrocyanide $Fe(CN)_6''''$, and ferricyanide $Fe(CN)_6'''$, ions respectively, which they yield in solution:

$$K_4[Fe(CN_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]''''; \quad K_3[Fe(CN)_6] \rightleftharpoons 3K^+ + [Fe(CN)_6]'''.$$

The ferrocyanide ion contains bivalent iron, while the ferricyanide ion contains trivalent iron. But neither of them responds to the test for iron and cyanide ions in solution.

Potassium ferrocyanide, $K_4Fe(CN)_6$, may be made adding excess of potassium cyanide to ferrous sulphate solution until the precipitate just redissolves—the solution deposits yellow crystals of potassium ferrocyanide on concentration: $FeSO_4 + 6KCN = K_4[Fe(CN)_6] + K_2SO_4$.

It is usually made from spent iron oxide of gas works (p. 840) containing Prussion blue. The spent oxide is boiled with milk of lime and filtered. The filtrate of calcium ferrocyanide, $Ca_2[Fe(CN)_6]$, is treated with potassium carbonate when calcium carbonate is precipitated and potassium ferocyanide remains in solution. $Ca_2[Fe(CN)_6] + 2K_2CO_3 = 2CaCO_3 + K_4Fe(CN)_6$.

The filtrate yields yellow crystals of potassium ferrocyanide or *yellow prussiate of potash,* $K_4Fe(CN)_6.3H_2O$ on evaporation.

When nitrogenous organic matter such as horn and leather clippings is fused with iron filings and potassium carbonate, and the mass boiled with water, the solution yields potassium ferrocyanide crystals on concentration.

With excess of ferric salt its solution gives a deep blue precipitate of ferric ferrocyanide, called Prussian blue—*a test for ferric iron.*

Potassium ferricyanide. $K_3Fe(CN)_6$, is made by oxidising potassium ferrocyanide with chlorine; $2K_4Fe(CN)_6 + Cl_2 = 2K_3[Fe(CN)_6] + 2KCl$.

Potassium chloride is separated by fractional crystallisation, and dark red crystals of potassium ferricyanide (*red prussiate of potash*) are obtained.

With excess of ferrous salt it gives a deep blue precipitate, called Turnbull's blue, which is identical with insoluble Prussian blue—*a test for ferrous iron.* Potassium ferricyanide is an oxidising agent.

Cobalt Co = 58·94.

Occurrence.—The chief cobalt ores are: *smaltite* or *speiss cobalt*, $CoAs_2$, *cobaltite or cobalt glance*, CoSAs, found in Ontario, Canada. Cobalt and nickel usually occur together.

Extraction.— The ore is roasted to remove As and S as volatile oxides, and is then smelted in a blast furnace with fuel and a flux of sand and limestone—two layers separate: iron passes into the slag in the upper layer, and cobalt and nickel arsenide settle at the bottom as *speiss*. The speiss is roasted with common salt. This operation eliminates the arsenic and converts the metals into the chlorides. The roasted mass is leached with water, and the copper is precipitated from the solution by scrap iron and the iron by bleaching powder and chalk. The precipitate is removed by filtration, and the cobalt is precipitated from the filtrate as hydroxide by adding more bleaching powder:

$$2CoCl_2 + 2Ca(OH)_2. + Ca(OCl)Cl + H_2O = 2Co(OH)_3 + 3CaCl_2.$$

Nickel in the filtrate may be precipitated as basic carbonate by sodium carbonate. The cobaltic hydroxide is ignited and the cobalt oxide Co_3O_4, formed is reduced to metal by heating with coke in the electric furnace. $Co_3O_4 + 4C = 3Co + 4CO$.

Cobalt is a silver white metal, closely resembling nickel.

Uses.— (i) In cobalt plating, (ii) In making *cobalt steel* (35 p.c.) used for permanent magnets, (iii) In making alloys such as *Festel metal* or *cochrome* (Cr, Fe, and Co) used for cutlery, and *stellite* (Co, Cr, and W) used for surgical instruments, and (iv) In making the blue pigment cobalt silicate, *smalt*.

Cobalt Compounds.—Cobalt forms *stable* cobaltous (bivalent Co) compounds—cobaltous salts form *pink* solutions; cobaltous salts show pink, *violet* or *blue* colour in the solid state. Cobaltic salts (trivalent Co) are very unstable—only few simple salts are known, e.g., CoF_3 and $Co_2(SO_4)_3$.

Cobaltous oxide, CoO, a green powder, is formed by heating hydroxide, carbonate or nitrate in absence of air, or by passing steam over red-hot cobalt: $H_2O + Co = H_2 + CoO$. When heated in air it forms Co_3O_4. It dissolves in acids to form cobaltous salts. It is used in making blue glass, glaze and enamels, and also for decorating chinaware blue.

Hydrated *cobaltic oxide*, Co_2O_3. is obtained as a black mass from cobalt solutions by hypochlorite.

Cobalto-cobaltic oxide, Co_3O_4, a black powder, is made by heating cobalt nitrate or any cobalt oxide in air.

Cobaltous hydroxide $Co(OH)_2$ is obtained as a rose-red precipitate by boiling cobaltous salt solution with alkali hydroxide—the precipitate dissolves in ammonia; the solution absorbs oxygen on exposure to air, forming a pink solution of a *cobaltammine* containing trivalent cobalt in a complex. There are some 2000 cobalt ammines known. $[Co(NH_3)_6]Cl_3$ is a typical example.

Cobaltous carbonate. $CoCO_3 . 6H_2O$ is obtained as a pink precipitate by the action of $NaHCO_3$ on cold cobaltous salt solution.

Cobaltous **chloride**, $CoCl_2,6H_2O$, **dark red deliquescent crystals, is made by dissolving the oxide or carbonate in hydrochloric acid and crystallising. It is used as a** ***sympathetic ink.*** **(p. 54).**

Cobaltous nitrate, $Co(NO_3)_2,6H_2O$, **is made in pink deliquescent crystals from a solution of the oxide, carbonate or the metal in dilute nitric acid.**

Cobalt nitrate solution is used in blowpipe analysis for Al (Thenard's blue). Zn (Rinman's green), and Mg.

Cobaltous sulphate, $CoSO_4$, $7H_2O$ is made in rose-red crystals from a solution of Co, oxide or carbonate in dilute sulphuric acid. It is isomorphous with green vitriol. It forms double salt with alkali sulphates, e.g., $K_2SO_4,CoSO_4,6H_2O$.

Cobaltous sulphide, CoS, is obtained as a black precipitate by passing H_2S through ammoniacal solution of cobaltous salt—it is not precipitated by H_2S from acid solution; but it is not soluble in dilute acids. It dissolves in strong HCl or aqua regia.

Complex cobaltic complex.— The most important cobaltic complexes are the *cobaltammines,* the *cobalticyanides* and the *cobaltinitrites.* The typical examples are: hexamine cobaltic chloride, $[Co(NH_3)_6]Cl_3$; potassium cobalticyanide, $K_3[Co(CN)_6]$; potassium cobaltinitrite, $K_3[Co(NO_2)_6]$.

Sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$, is formed by adding 50 per cent acetic acid to a solution of cobalt nitrate and sodium nitrite; it is precipitated by alcohol:

$$Co(NO_3)_2+5NaNO_2+2HNO_2 = Na_3[Co(NO_2)_6]+2NaNO_3+NO+H_2O.$$

Sodium cobaltnitrite solution is a reagent for potassium salt with which it gives a yellow precipitate of potassium cobaltinitrite.

Detection of cobalt.—*Dry test.*—(i) A cobalt compound, when heated with sodium carbonate on charcoal in a reducing flame, yields a grey, feebly magnetic mass. (ii) Cobalt compounds give beautiful blue borax bead both in oxidising and reducing flames.

Wet tests.—Solution of cobal salt (i) gives a black precipitate of CoS when H_2S is passed into its ammoniacal solution; (ii) forms a yellow precipitate of potassium cobalti nitrite $K_3[Co(NO_2)_6]$ with potassium nitrite in presence of excess acetic acid (distinction from Ni); (iii) forms a blue *upper layer* on adding ammonium sulphocyanide and shaking with amyl alcohol and ether (*distinction from nickel*).

Nickel Ni = 58·69

Occurrence.—Metallic nickel is found with iron in meteorities. Chief nickel ores are: *pentlandite* (Ni, Cu, Fe)S, found in Sudbury, Ontario, and *garnierite* $(Ni,Mg)SiO_3,xH_2O$, found in New Caledonia. Other ores are: *smaltite* $(Ni,Co,Fe)As_2$, *niccolite* NiAs, *millerite* NiS, *nickel glance* NaAsS, and *nickel bloom* $Ni_3(AsO_4)_2$, H_2O.

Metallurgy.—The Sudbury ore is sulphides of Ni, Cu and Fe, and contains about 2·5 p.c. Ni, 1·5 p.c. Cu, and the precious metals Ag, Au and Pt, etc. The ore is concentrated by floatation, and the iron is then removed by *selective oxidation,* exactly as in metallurgy of copper; for this the ore is (i) *roasted,* (ii) *smelted* with fuel (coke) and flux (silica) in a blast furnace to a slag of ferrous silicate and a *crude matte* of nickel and copper sulphides, still containing some iron; the latter is therefore (iii) *bessemerised,* giving a slag of ferrous silicate and a *refined matte* of Cu_2S and NiS (composition 56 Ni, 24-30 Cu, 0·1—0·5 Fe, 14—7 S). The refined matte is either roasted and reduced with coke in an electric furnace to **monel metal** (Ni 67, Cu 28, Fe and Mn 5) or worked for nickel by:

(a) The Mond process which depends on the formation and subsequent decomposition of volatile nickel carbonyl: $Ni+4CO \rightleftharpoons Ni(CO)_4$.

(i) The refined matte is *roasted* to oxides and leached with hot dilute H_2SO_4 which dissolves out most of the copper oxide but not the nickel oxide, which remains insoluble.

(ii) The *oxides of* Ni and Cu are then reduced at 300° to 350° to finely divided Ni and Cu by the hydrogen in water gas, which is thus enriched in CO. $NiO+H_2 = Ni+H_2O$; $CuO+H_2 = Cu+H_2O$.

(iii) The nickel is then *volatalised* at 60°C in a current of CO (the enriched water gas from operation (ii) above, is used) as nickel carbonyl—copper does not form carbonyl.

(iv) The nickel carbonyl is then *decomposed* into Ni and CO at 180°C in contact with fine nickel granules—nickel is deposited on the granules, and CO is used over again for volatilisation in operation (iii). The nickel is 99·8% pure. The residue in the volataliser contains the precious metals Ag, Au, Pt, etc. Copper sulphate is a by-product.

(b) **The Orford process** in which the matte is smelted with coke and salt-cake which forms sodium sulphide, and poled when two layers separate—the top layer of sodium and cuprous sulphides, and the bottom layer of nickel sulphide which is separated, roasted to the oxide and reduced to nickel by heating with charcoal.

Nickel is refined by electrodeposition from nickel ammonium sulphate solution with a crude nickel block as anode and a pure sheet of Ni as cathode. The same process is used in nickel plating. Nickel plating readily tarnishes in town air.

Properties.—Nickel is a greyish-white, hard but malleable metal capable of taking high polish. It resembles iron, thus it is attacked by steam or dilute acids but is unattacked by molten alkalis; concentrated nitric acid renders it passive. *But it does not rust,* and hence its use for electroplating. Nickel is slightly magnetic.

$$Ni+H_2O \rightleftharpoons NiO+H_2; \quad Ni+2HCl = NiCl_2+H_2.$$

Uses.—(i) In electroplating, (ii) In making crucibles, tongs, and utensils for dairies, (iii) As a catalyst in hydrogenation of oils, and (v) In making alloys: *German silver and monel metal* (p. 457), *nichrome* (p. 487), *nickel steel* with 35 p.c. Ni, very low coefficient of thermal expansion, used in making pendulum, and measuring instruments), *nickel coins* (Ni 25 Cu 75).

Nickel Compounds.—Nickel forms stable nickelous salts (bivalent Ni) which give *green solutions.* Nickelic salts (trivalent Ni) are unknown (cf. Fe and Co).

Nickel monoxide, NiO, a green powder, prepared as CoO. With acids it forms nickelous salts.

Nickelic oxide, Ni_2O_3, a black powder, made as Co_2O_3. It liberates chlorine from hydrochloric acid. $Ni_2O_3+6HCl = 2NiCl_2+3H_2O+Cl_2$.

Nickel Hydroxide, $Ni(OH)_2$. It is insoluble in alkali hydroxide but disoslves in ammonia or ammonium salt solution to a blue solution—the solution is not oxidised by air or H_2O_2 (difference from cobalt).

Nickel carbonate, $NiCO_3,6H_2O$, green, made as cobalt carbonate.

Nickel chloride, $NiCl_2$, $6H_2O$, green deliquescent crystals, made from a solution of nickel in aqua regia or the oxide in HCl.

Nickel sulphate, $NiSO_4,7H_2O$, green rhombic prisms, resembles cobalt sulphate $CoSO_4$, $7H_2O$ and also made similarly. It forms the double salt nickel ammonium sulphate, $NiSO_4,(NH_4)_2SO_4,6H_2O$.

Nickel nitrate, $Ni(NO_3)_2, 6H_2O$, green deliquescent crystals, made as cobalt nitrate.

Nickel sulphide, NiS, black, resembles CoS and also obtained similarly.

Nickel carbonyl, $Ni(CO)_4$, a colourless poisonous liquid, b.p. 43·2° and m. p. −25°, is made by passing CO over finely divided Ni at 30° $Ni + 4CO \rightleftharpoons Ni(CO)_4$. When pure, the carbonyl explodes at 60°. $Ni(CO)_4 = Ni+2CO_2+2C$, but when diluted with CO it decomposes reversibly by heat. $Ni(CO)_4 \rightleftharpoons Ni + 4CO$.

Detection of nickel.—Dry tests: (a) *Blowpipe test.*—Nickel compounds when heated with sodium carbonate on charcoal give a grey mass of slightly magnetic nickel. (b) *Borax bead test.*—The bead is coloured *brown* in oxidising flame, and *grey* in reducing flame.

Wet tests.— Solution of a nickel salt (i) gives a black precipitate of NiS when H_2S is passed into the ammoniacal solution. (ii) gives a red precipitate of nickel dimethyl gyloxime on warming when an alcoholic solution of dimethylglyoxime is added to the ammoniacal solution (*difference from Co*). *This is a delicate test for nickel.* The precipitate is filtered, washed, dried at 110°—120°C, and weighed for estimation of nickel.

Separation of nickel and cobalt—The metals are precipitated in group IIIB as the sulphides which are dissolved by heat in aqua regia or in strong HCl containing $KClO_3$; the solution is evaporated to dryness and the residue dissolved in water. Potassium cyanide is then carefully added to the solution until the precipitate first formed just redissolves. The solution contains potassium cobaltocyanide and nickelocyanide: $CoCl_2 + 6KCN = K_4[Co(CN)_6] + 2KCl$.

$$NiCl_2 + 4KCN = K_2[Ni(CN)_4] + 2KCl.$$

On warming the solution with sodium hypobromite (bromine and caustic soda) the nickelocyanide is decomposed, forming a black precipitate of hydrated nickel dioxide, NiO_2, mainly, while the cobaltocyanide is oxidised to the cobalticyanide and remains in solution.

$$K_2[Ni(CN)_4]+2NaOH+O = 2KCN+2NaCN+NiO_2+H_2O$$

$$2K_4[Co(CN)_6]+H_2O+O = 2K_3[Co(CN)_6]+2KOH$$

Exercises

1. Name the important ores of iron. Describe the process of making pig iron, stating the main reactions that occur. *U. P. Board* '45.

Explain the changes involved, if any, when a piece of iron is dipped in (a) strong nitric acid, (b) a solution of copper sulphate, (c) a solution of ferric chloride containing hydrochloric acid. *Calcutta* '45.

2. What is the difference in composition between cast iron, wrought iron and steel? Describe their properties and uses. How is steel manufactured by the Bessemer process? *Madras* '49.

Given metallic iron, how would you prepare from it ferrous sulphate, ferric chloride, magnetic oxide of iron and ferric oxide? *Calcutta* '59.

3. Describe the preparation of specimens of anhydrous ferrous and ferric chlorides from iron. How is green vitriol obtained commercially, and what is the action of heat upon it. How would you distinguish between ferrous and ferric iron? How would you obtain ferric chloride from ferrous sulphate?

4. State what changes occur when (i) nitric oxide is passed into ferrous sulphate solution, (ii) strong sulphuric acid is cautiously added to a solution containing sodium nitrate and ferrous sulphate, (iii) ferrous sulphate solution is boiled with strong sulphuric acid, (iv) hydrogen sulphide is passed into ferric chloride solution, (v) ferric chloride solution is treated with sodium carbonate (vi) ferrous chloride solution is saturated with chlorine, (vii) a solution of ferrous sulphate is left exposed to air, (viii) ferric oxide is strongly heated with sodium carbonate.

5. Describe the manufacture of steel from pig iron. What are (a) mild steel, (b) hard steel (c) alloy steels? Give the composition and uses of alloy steels. *Punjab* '48.

XXXIV

Chromium and Manganese

Chromium and manganese are tearnsitional elements (p. 163).

	At. no.	At. wt.	Density	At.-vol.	M. pt. °C	B. pt. °C
Chromium	24	52·01	6·74	7·7	1800°	2200°
Manganese	25	54·93	7·39	7·4	1260°	1900°

They exhibit *variable valency* and give *colouerd ions*—bivalent chromous ion is *blue*, and manganous ion *pink*, whereas trivalent chormic ion is *green* and manganic ion *violet*. Chromous salts are very unstable and are oxidised to stable chromic salts more readily than ferrous salts. Manganous salts are stable, like cobaltous salts, while manganic salts are extremely unstable.

Their higher oxides are *acidic*, thus CrO is basic, Cr_2O_3 amphoteric and CrO_3 acidic, while MnO and Mn_2O_3 are basic, MnO_2 amphoteric, MnO_3 and Mn_2O_7 acidic. Chromates are isomorphous with manganates, e.g., K_2CrO_4 and K_2MnO_4.

Acidity of their higher oxides provides the only excuse for their classification with sulphur and chlorine. Thus both CrO_3 and SO_3 are acidic, and the chromate, e.g., K_2CrO_4, and sulphate, e.g., K_2SO_4, are isomorphous. Mn_2O_7 is acidic and explosive like Cl_2O_7, and perchlorates and permanganates are isomorphous, e.g., $KClO_4$ and $KMnO_4$.

Chromium Cr = 52·01

Occurrence.— The principal ore of chromium is **chromite** or **chrome iron stone** which is ferrous chromite $FeCr_2O_4$ or FeO, Cr_2O_3. It is mined in South Africa, Russia, India and other places.

Chromite is highly refractory and is made into chrome bricks for furnace linings. Most chromium compounds and the alloy *ferrochrome* are made from it.

Extraction.—Metallic chromium is made from chromic oxide Cr_2O_3 by the thermite process: $Cr_2O_3+2Al=2Cr+Al_2O_3+120{,}000$ cals.

A mixture of dry chromic oxide and aluminium powder is taken in a refractory crucible, and a cartridge of barium peroxide and magnesium powder, provided with a fuse of magnesium ribbon, is inserted in the mixture. The reaction is started by igniting the magnesium ribbon. The 'thermit' reaction evolves so much heat that the chromium melts and collects as a liquid under the alumina.

Properties.— (i) Chromium is a hard but malleable bluish white metal that *does not tarnish in air,* and hence its use in *chromium plating*.

(ii) It decomposes steam at red heat: $2Cr+3H_2O \rightleftharpoons Cr_2O_3+3H_2$.

(iii) It dissolves slowly in dilute acids, giving hydrogen and a chromous salt: $Cr+2HCl = CrCl_2+H_2$.

Concentrated sulphuric acid attacks chromium, forming the sulphate and sulphur dioxide. Concentrated nitric acid renders chromium *passive* (cf. iron).

Uses of chromium.—Chromium finds uses in (i) *special steel industry*, and is employed in the form of the alloy 'ferro chrome' of 60—70 p.c. chromium with iron, made by reducing chromite with coke in an electric furnace.

$$FeCr_2O_4 + 4C = Fe + 2Cr + 4CO.$$

Chromium steel is extremely hard and tough, and is used in making armour plates, cutting tools, etc. *Stainless steel* is ordinary steel with 12—14 p.c. of chromium, extensively used in cutlery. Steels with 17—18 p.c. of chromium and 7 p.c. or more of nickel have superior corrosive resistance. *Chromium vanadium steel* is extremely hard, and is used in locomotive wheels, axle shafts, etc. *chromium tungsten steel* is used for high speed tools.

(ii) *Making alloys.*—The alloy nichrome (Ni 60, Fe 25, Cr 15) has a high resistance, and is used for resistance heaters.

(iii) *Chromium plating.*—Chromium is deposited electrolytically from a solution of chromic acid in sulphuric acid—chromium plating resists wear and corrosion extremely well, and is silver-white in colour.

Chromium Compounds.—Chromium forms the oxides : CrO, Cr_2O_3, and CrO_3.

(i) **Chromous oxide,** CrO, strongly basic, forms, *unstable* chromous salts, usually *blue* in colour, containing bivalent chromium, and resembling ferrous and manganous salts. *Chromous salts are readily oxidised to the chromic state,* and hence they are reducing agents.

(ii) **Chromic oxide,** Cr_2O_3, green in colour, weakly basic and amphoteric, forms stable chromic salts, *violet* or *green* in colour, containing trivalent chromium and resembling ferric salts.

(iii) **Chromium trioxide,** CrO_3, dark-red in colour, strongly acidic, forms *yellow chromates*, and *orange-red dichromates*, containing hexavalent chromium.

Chromous chloride.— Anhydrous chromous chloride, $CrCl_2$, is made as white crystals by passing HCl gas over metallic chromium. Chromous chloride in solution is obtained by reducing a chromium compound with zinc and hydrochloric acid in absence of air ;

$$K_2Cr_2O_7 + 8HCl + 6H = 2KCl + 2CrCl_3 + 7H_2O$$

$$CrCl_3 + H = CrCl_2 + HCl$$

On adding zinc and concentrated hydrochloric acid to the orange-red solution of potassium dichromate, the liquid first becomes green ($CrCl_3$) and then blue ($CrCl_2$). The blue solution thus prepared is added to a saturated solution of sodium acetate, when a red precipitate of chromous acetate is produced.

The chromous acetate is dissolved in ice-cold concentrated HCl in a flask from which the air is expelled by hydrogen, and a current of HCl gas passed into the solution, when a blue precipitate of chromous chloride, $CrCl_2,4H_2O$, is thrown down.

It is a strong reducing agent, and is readily oxidised in air to chromic chloride. It liberates hydrogen from an acid solution:

$$2CrCl_2 + 2HCl \rightleftharpoons 2CrCl_3 + H_2$$

Chromous sulphate, $CrSO_4, 7H_2O$, isomorphous with ferrous sulphate, is obtained in blue crystals by dissolving the chromous acetate or the metal in dilute H_2SO_4 and cooling. Like the chloride, it is a reducing agent.

Chromous oxide, CrO, is formed as a black powder by exposing chromium amalgam in air. Chromous hydroxide formed as a brownish-yellow mass by adding caustic soda to a solution of chromous salt, yields chromic oxide on heating : $2Cr(OH)_2 = Cr_2O_3 + H_2O + H_2$.

Chromic oxide, Cr_2O_3, isomorphous with Al_2O_3 and Fe_2O_3 is formed as a green powder by igniting chromic hydroxide or ammonium dichromate.

$$(NH_4)_2Cr_2O_7 = N_2 + 4H_2O + Cr_2O_3.$$

The ignited oxide is insoluble in acids, but it may be converted to sodium chromate by fusion with sodium peroxide.

$$Cr_2O_3 + 3Na_2O_2 + H_2O = 2Na_2CrO_4 + 2NaOH$$

Chromic oxide is used as green oil paint under the name chrome green. This is also used in tinting glass and porcelain. *Guignet's green,* $Cr_2O_3,2H_2O$, a pigment, is obtained by fusing potassium dichromate with boric acid.

Chronic hydroxide, $Cr(OH)_3$, is formed as a pale green gelatinous precipitate by the action of alkali hydroxide or ammonia on the solution of a chromic salt :

$$CrCl_3 + 3NH_4OH = Cr(OH)_3 + 3NH_4Cl.$$

It is readily converted to chromate on treatment with sodium peroxide or bromine in presence of alkali : $2Cr(OH)_3+3Na_2O_2 = 2Na_2CrO_4+2NaOH+2H_2O$.

Chromic chloride, $CrCl_3$, is made in the anhydrous state by passing chlorine over a heated mixture of chromic oxide and coke:

$$Cr_2O_3+3Cl_2+3C = 3CO+2CrCl_3$$

The crystals thus prepared are insoluble in water and even in boiling concentrated sulphuric acid, but readily dissolve in water in presence of a trace of reducing agent such $CrCl_2$, $SnCl_2$, etc., giving a green solution.

A green solution of chromic chloride may be made by boiling chromic acid, CrO_3, with concentrated hydrochloric acid:

$$2CrO_3+12HCl=2CrCl_3+3Cl_2+6H_2O.$$

The solution deposits green crystals of the hydrate, $CrCl_3,6H_2O$, on crystallisation. The hydrate exists in three forms: (i) violet $[Cr(H_2O)_6]Cl_3$; (ii) light green $[Cr(H_2O)_5Cl]Cl_2.H_2O$; (iii) dark green $[Cr(H_2O)_4Cl_2]Cl.2H_2O$.

Chromic sulphate, $Cr_2(SO_4)_3$, $18H_2O$, is obtained in violet octahedral crystals by dissolving chromic hydroxide with concentrated sulphuric acid, and allowing the green solution to stand.

Chrome alum, $K_2SO_4,Cr_2(SO_4)_3,24H_2O$, made by reducing potassium dichromate acidified with sulphuric acid with sulphur dioxide or alcohol; $K_2Cr_2O_7+H_2SO_4+3SO_2 = K_2SO_4+Cr_2(SO_4)_3+H_2O$.

Potassium dichromate is dissolved in hot water, and then cooled and acidified with a little concentrated sulphuric acid. Sulphur dioxide is passed into the well-cooled solution until the colour changes from orange-red to green. Violet octahedral crystals of chrome alum deposit on standing.

Chrome alum is used in dyeing, calico-printing, and in chrome-tanning.

Chromium trioxide, CrO_3, is made by adding concentrated sulphuric acid to saturated solution of potassium dichromate. The dark red crystals of chromium trioxide deposit, and are filtered through asbestos.

$$K_2Cr_2O_7 + 2H_2SO_4 = 2KHSO_4 + 2CrO_3 + H_2O.$$

Chromium trioxide is sometimes called 'chromic acid' (of which it is the anhydride; H_2CrO_4 is unknown). Its aqueous solution is red and strongly acid. It decomposes by strong heat, giving off oxygen : $4CrO_3 = 2Cr_2O_3 + 3O_2$.

An acidic oxide, it forms two series of salts, the *chromates* (e.g. K_2CrO_4) and *dichromates* (e.g. $K_2Cr_2O_7$), analogous to sulphates and disulphates.

Chromates and dichromates.— These most important compounds of chromium are obtained directly from chromite. A mixture of finely powdered chromite, sodium carbonate and quicklime is heated to redness in a reverberatory furnace *with free admission of air,* when the chromium is oxidised to sodium chromate (yellow in colour) and the iron to ferric oxide—the addition of lime keeps the mass porous and prevents fusion.

$$4FeCr_2O_4+8Na_2CO_3+7O_2 = 8Na_2CrO_4+2Fe_2O_3+8CO_2.$$

The sodium chromate is extracted with water, and the solution is acidified with concentrated sulphuric acid. The sodium sulphate separates and is removed.

$$2Na_2CrO_4 + H_2SO_4 = Na_2SO_4 + Na_2Cr_2O_7 + H_2O.$$

The solution is concentrated, when deliquescent red crystals of sodium dichromate, $Na_2Cr_2O_7,2H_2O$ are deposited.

Potassium dichromate, $K_2Cr_2O_7$, being less soluble than the sodium salt, is made by adding KCl to sodium dichromate solution—potassium dichromate deposits first in red crystals.

$$Na_2Cr_2O_7 + 2KCl = K_2Cr_2O_7 + 2NaCl.$$

Potassium chromate, K_2CrO_4, is made by adding calculated amount of potassium hydroxide or carbonate to a solution of potassium dichromate—the solution on concentration yields lemon yellow crystals of K_2CrO_4, isomorphous with K_2SO_4.

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

Both potassium chromate and potassium dichromate are non-deliquescent and crystallise without water of crystallisation. Sodium chromate $Na_2CrO_4,10H_2O$ and sodium dichromate, $Na_2Cr_2O_7,2H_2O$, are both deliquescent. Potassium dichromate is moderately soluble in cold water, and freely soluble in hot water.

Chromates and dichromates are used as oxidising agents, as mordants in dyeing, in chrome-tanning, and in making pigments.

Potassium dichromate is a valuable oxidisng agent in volumetric analysis. In acid solution it yields 3 atoms of oxygen per molecule, thus :

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O.$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI = 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O.$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$$

Ammonium dichromate, $(NH_4)_2Cr_2O_7$, is made by adding ammonia to requisite quantity of chromium trioxide in solution. It forms orange crystals which decompose on heating : $(NH_4)_2Cr_2O_7 = N_2 + 4H_2O + Cr_2O_3$.

Lead chromate, $PbCrO_4$, is made by mixing a solution of a lead salt with that of a chromate. It is insoluble in water; a bright yellow powder much used as a pigment under the name of '*chrome yellow*'. Basic lead chromate $PbCrO_4$, PbO is the red pigment '*chrome red*'; mixed with lead chromate it forms *chrome orange*.

Chromyl chloride, CrO_2Cl_2, is obtained as a dark red liquid by distilling a mixture of potassium dichromate and sodium chloride with concentrated sulphuric acid.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 = 2CrO_2Cl_2 + 2KHSO_4 + 4NaHSO_4 + 3H_2O.$$

Bromides and iodides, however, do not form similar volatile chromium compounds but liberate free halogens, when heated with $K_2Cr_2O_7$ and H_2SO_4.

The reaction is, therefore, used to detect a chloride in presence of bromides and iodides—the distillate (of CrO_2Cl_2) is collected in NaOH solution when it is hydrolysed to sodium chromate : $4NaOH + CrO_2Cl_2 = Na_2CrO_4 + 2NaCl + 2H_2O$.

The sodium chromate solution acidified with acetic acid, gives a yellow precipitate of lead chromate with lead acetate solution.

Chromyl chloride is readily hydrolysed by water :

$CrO_2Cl_2 + H_2O = CrO_3 + 2HCl$. It is an oxidising agent.

Chromic sulphide, Cr_2S_3, is made by heating sulphur with chromium or $CrCl_3$ in H_2S. It is not formed by the action of ammonium sulphide on chromic salts, only chromic hydroxide is precipitated (*cf.* Al_2S_3).

$$CrCl_3 + 3(NH_4)_2S + 6H_2O = 2Cr(OH)_3 + 6NH_4Cl + 3H_2S.$$

Detection of chromium.— (i) *Borax bead test.*—The presence of chromium is indicated by the *green* colour of the bead.

(ii) *Fusion test.*—A mixture of a chromium compound with sodium carbonate and a crystal of KNO_3 or with sodium peroxide, on being strongly heated on a piece of broken porcelain, forms a *yellow* melt which contains sodium chromate. The fused mass is extracted with water—the yellow solution of Na_2CrO_4 is acidified with acetic acid and treated with lead acetate when a yellow precipitate of $PbCrO_4$ is formed: $Cr_2O_3 + 3Na_2O_2 + H_2O = 2Na_2CrO_4 + 2NaOH$.

(iii) *Perchromic acid test.*—A cold solution of a chromate acidified with dilute H_2SO_4 is covered with ether and hydrogen peroxide is added, and the mixture shaken, when the ether layer assumes a deep blue colour owing to the formation of perchromic acid, CrO_3, which dissolves in ether.

Manganese Mn = 54·93.

Occurrence.—The principal ore of manganese is **pyrolusite,** manganese dioxide, MnO_2. It is usually contaminated with ferric oxide. Next to Russia, India is the biggest producer of pyrolusite. Less important minerals are *braunite*, Mn_2O_3; manganite, Mn_2O_3, H_2O, and *hausmannite*, Mn_3O_4.

Preparation.—Impure manganese, containing carbon, is made by strongly heating the oxide Mn_3O_4 with carbon:

$$Mn_3O_4 + 4C = 3Mn + 4CO.$$

A purer metal is obtained by the thermite process. Manganese dioxide is heated to redness to yield the oxide Mn_3O_4. This is mixed with aluminium powder and ignited in a crucible (*cf.* chromium. p.486): $3Mn_3O_4 + 8Al = 4Al_2O_3 + 9Mn$.

Properties.—(i) Manganese is a greyish-white, hard and brittle metal with a high m.p. of 1260°.

(ii) It is not easily oxidised in air unless it contains carbon or is finely divided—the finely divided metal burns in air.

(iii) Unless quite pure, it decomposes cold water, giving off hydrogen: $Mn + 2H_2O = Mn(OH)_2 + H_2$. The pure metal is only slightly attacked by steam.

(iv) It dissolves in dilute acids (even in dilute nitric acid) giving off H_2 and yielding manganous salts: $Mn + 2HCl = MnCl_2 + H_2$.

(v) It combines with nitrogen above 1200° forming nitride and with carbon in the electric furnace, yield the carbide Mn_3C.

Uses of manganese.—The metal is mainly used in steel industry in making alloy steels and as a deoxidiser. It is added to the steel in the form of *ferro-manganese* and *spiegeleisn.*

Ferro-manganese, an alloy of Fe and Mn (70—80 p.c. Mn) is obtained by smelting a mixture of iron and manganese ores with carbon in the blast furnace Spiegeleisn, also an alloy of Fe and Mn, contains 20—30 p.c. Mn only.

Manganese steel, containing up to 13 p.c. Mn, is extremely hard and tough, and is used in making jaws of rock-crushers. *Manganin* is an alloy of copper 82—84, manganese 12—15, and nickel 2—4, and is used for resistance coils since its electrical resistance is very slightly affected by temperature. *Manganese bronze,* an alloy of Cu 55—65, Zn 30—45, Fe 0·5—2, and Mn and Al 0·2—4, is used for making propeller blades, because of its stability towards sea-water.

Manganese Compounds.—Manganese forms the oxides : MnO, Mn_2O_3, Mn_3O_4, MnO_2, MnO_3 and Mn_2O_7.

Manganous oxide, MnO, *strongly basic*, forms the *stable* manganous salts, e.g., $MnCl_2$ and $MnSO_4$, in which the metal is bivalent, and which are similar to ferrous and chromous salts except that they are not at all easily oxidised to manganic salts. Hydrated manganous salts are *pink* in colour.

Manganic oxide, Mn_2O_3, basic, forms *unstable* manganic salts, e.g., $Mn_2(SO_4)_3$, in which the metal is trivalent, and which are similar to ferric and chromic salts.

Mangano-manganic oxide, Mn_3O_4, is a mixed oxide of MnO and Mn_2O_3.

Manganese dioxide, MnO_2, *weakly acidic*, contains tetravalent manganese, and forms manganites, such as $CaMnO_3$.

Manganese trioxide, MnO_3, *acidic*, contains hexavalent manganese, and forms manganates, such as Na_2MnO_4, isomorphous with sulphates.

Manganese heptoxide, Mn_2O_7, *acidic*, contains heptavalent manganese and gives rise to permanganates such as $KMnO_4$, which are isomorphous with perchlorates.

The basic character of the oxides of manganese progressively decreases with the increasing valency of the metal (*vide* p. 177).

Manganous oxide, MnO, an olive-green powder, made by heating a higher oxide of manganese in hydrogen : $MnO_2 + H_2 = MnO + H_2O$. It is basic and forms manganous salts with acids.

Manganous hydroxide, $Mn(OH)_2$, is obtained as a white precipitate by the action of alkali on manganous chloride or sulphate solution. It quickly absorbs atmospheric oxygen to form brown manganic hydroxide.

$$2Mn(OH)_2 + O = 2MnO(OH) + H_2O.$$

Manganous carbonate. $MnCO_3$, is formed as a white or pale buff-coloured precipitate by adding sodium carbonate to a manganous salt solution. It decomposes on heating to manganous oxide : $MnCO_3 = MnO + CO_2$. It is sparingly soluble in water containing CO_2, forming bicarbonate.

$$MnCO_3 + H_2O + CO_2 = Mn(HCO_3)_2.$$

Manganous chloride, $MnCl_2$, is made by boiling pyrolusite with strong hydrochloric acid till no more chlorine is evolved:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The solution usually contains ferric chloride which is precipitated as ferric hydroxide by adding precipitated manganous carbonate:

$$2FeCl_3 + 3MnCO_3 + 3H_2O = 2Fe(OH)_3 + 3MnCl_2 + 3CO_2.$$

The filtrate is concentrated when pink monoclinic crystals of $MnCl_2,4H_2O$ separate. It may also be made by heating pyrolusite with ammonium chloride, and extracting with hot water and crystallising. Manganous chloride is deliquescent and highly soluble in water. $3MnO_2 + 6NH_4Cl = 3MnCl_2 + N_2 + 4NH_3 + 6H_2O$.

Manganous sulphate, $MnSO_4$, is made by heating pyrolusite with concentrated sulphuric acid: $2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$.

The solution is evaporated to dryness, and the residue is heated to decompose the ferric sulphate: $Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$. The residue is extracted with water; the filtrate on concentration yields pink monoclinic efflorescent crystals of $MnSO_4, 4H_2O$.

There are several hydrates. $MnSO_4,7H_2O$ is isomorphous with $FeSO_4,7H_2O$, and $MnSO_4,5H_2O$ is isomorphous with blue vitriol $CuSO_4,5H_2O$.

Manganous nitrate, $Mn(NO_3)_2$, is formed by dissolving manganous carbonate in dilute nitric acid. On evaporation pink deliquescent crystals of $Mn(NO_3)_2$, $6H_2O$ separate. It decomposes on heating : $Mn(NO_3)_2 = MnO_2 + 2NO_2$.

Manganous sulphide, MnS, is formed as a pale pink or buff precipitate by passing H_2S into a neutral or alkaline solution of manganous salt. It dissolves in dilute acids, even acetic acid.

Manganic oxide, Mn_2O_3, is formed as a brown powder by heating MnO or MnO_2 to redness in air. It is a weakly basic oxide and dissolves in hydrochloric [illegible] sulphuric acids, forming manganic salts. With hot dilute nitric acid it gives manganous nitrate and manganese dioxide :

$$Mn_2O_3 + 2HNO_3 = Mn(NO_3)_2 + H_2O + MnO_2.$$

Manganic hydroxide, MnO(OH), is formed as a brown powder by the action of chlorine on manganous carbonate suspended in water.

$$3MnCO_3 + Cl_2 + H_2O = 2MnO(OH) + MnCl_2 + 3CO_2.$$

The excess of manganous carbonate is removed by treatment with dilute nitric acid.

Mangano manganic oxide, Mn_3O_4, is made by *strongly* heating any oxide of manganese in air : $3MnO_2 = Mn_3O_4 + O_2$; Mn_2O_3 is formed at a lower temperature. It dissolves in cold concentrated sulphuric acid to a red solution of manganous and manganic salts : $Mn_3O_4 + 4H_2SO_4 = MnSO_4 + Mn_2(SO_4)_3 + 4H_2O$.
Hot dilute HNO_3 forms manganous nitrate and manganese dioxide :

$$Mn_3O_4 + 4HNO_3 = 2Mn(NO_3)_2 + MnO_2 + 2H_2O.$$

Manganic salts.— These salts are markedly *unstable*. The brown solution of MnO_2 in cold concentrated HCl contains magnanic chloride $MnCl_3$ which decomposes on heating : $2MnO_2 + 8HCl = 2MnCl_3 + 4H_2O + Cl_2$.

$$2MnCl_3 = 2MnCl_2 + Cl_2.$$

Manganic sulphate, $Mn_2(SO_4)_3$ is formed as a green solid by heating MnO_2 with concentrated sulphuric acid at 138°C. It forms *alums* isomorphous with common alums. $4MnO_2 + 6H_2SO_4 = 2Mn_2(SO_4)_3 + 6H_2O + O_2$.

Manganese dioxide, MnO_2. It occurs in nature as *pyrolusite.* Pure manganese dioxide is obtained by heating manganous nitrate till brown fumes appear: $Mn(NO_3)_2 = MnO_2 + 2NO_2$.

It is feebly acidic, forming manganites with strong bases, eg., $CaMnO_3$: it may also be regarded as the basic oxide of very unstable salts $MnCl_4$ and $Mn(SO_4)_2$.

It is an oxidising agent and forms Mn_3O_4 by strong heat: $3MnO_2 = Mn_3O_4 + O_2$. With hot and strong HCl, it yields chlorine:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

With hot and strong H_2SO_4 it yields manganic sulphate and oxygen below 140°C, but at higher temperature, manganous sulphate is formed. $4MnO_2 + 6H_2SO_4 = 2Mn_2(SO_4)_3 + 6H_2O + O_2$

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

Pyrolusite usually contains ferric oxide as an impurity. The manganese dioxide content of a sample of pyrolusite is estimated by heating it with strong HCl, and passing the chlorine that is liberated into potassium iodide solution. $2KI + Cl_2 = 2KCl + I_2$. The liberated iodine is subsequently titrated against standard sodium thiosulphate solution.

In presence of dilute H_2SO_4, MnO_2 oxidises ferrous sulphate to ferric sulphate and oxalic acid $H_2C_2O_4$, into carbon dioxide—both tht reactions are used for the valuation of pyrolusite.

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O.$$

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O.$$

Besides its use as a decolouriser in glass, manganese dioxide is used as a depolariser in Leclanche cells, as a drier for paint.

Manganese heptoxide, Mn_2O_7, a brown oily liquid which gives a violet vapour, is formed by careful addition of powdered $KMnO_4$ to ice-cold concentrated sulphuric acid. $2KMnO_4 + 2H_2SO_4 = 2KHSO_4 + M_2O_7 + H_2O$.

It *explodes violently* on warming ; it forms a violet solution of permanganic acid with water : $Mn_2O_7 + H_2O = 2HMnO_4$. Manganeso trioxide, MnO_3, is unknown.

Potassium permanganate, $KMnO_4$.—When manganese dioxide is fused with a mixture of caustic potash and an oxidising agent such as potassium chlorate, a *green* mass of potassium manganate is formed: $2MnO_2 + 4KOH + O_2 = 2K_2MnO_4 + 2H_2O$.

The potassium manganate is hydrolysed with water, giving a *purple* solution of potassium permanganate.

$$3K_2MnO_4 + 2H_2O \rightleftharpoons 2KMnO_4 + 4KOH + MnO_2.$$

The hydrolysis occurs readily by passing CO_2 into the solution when the potassium hydroxide is removed as potassium bicarbonate.

$$3K_2MnO_4 + 2H_2O + 4CO_2 = 2KMnO_4 + 4KHCO_3 + MnO_2.$$

Expt.—Finely powdered pyrolusite (2 parts) is stirred with an iron rod into a fused mixture of potassium hydroxide (2 parts) and potassium chlorate (1 part) on an iron sand-bath. The mixture is heated until the mass stiffens. The mass is then cooled, ground to powder, and extracted with water. The solution is boiled and carbon-dioxide is passed in until the solution assumes a deep-purple colour. The purple solution of potassium permanganate is filtered through *asbestos*, concentrated, and allowed to crystallise, when potassium permanganate deposits in purple prisms.

On a technical scale finely ground pyrolusite is fused with caustic potash in a muffle furnace with circulation of air—the resulting fused mass in leached with water and the alkaline leach of potassium manganate is converted to permanganate : (i) by electrolytic oxidation with a rotating anode of iron : $2K_2MnO_4 + H_2O + O = 2KMnO_4 + 2KOH$ or (ii) by passing CO_2 into the solution, as above, or (iii) by chlorine into the solution,—$KMnO_4$, being less soluble than KCl, separates first on fractional crystallisation :

$$2K_2MnO_4 + Cl_2 = 2KCl + 2KMnO_4.$$

Potassium permanganate is isomorphous with potassium perchlorate, $KClO_4$. Potassium permanganate is moderately soluble in water, giving a deep purple solution. It evolves oxygen on heating: $2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$. *It is a powerful oxidising agent*—the oxidising action is different in acid or alkaline solution.

(i) **In acid solution.**— In presence of dilute sulphuric acid potassium permanganate is reduced to manganous salt and 5 atoms of available oxygen are obtained from 2 molecules of permanganate :

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

In acid solution it reacts *quantitatively* with reducing agents, as follows : Ferrous salts are oxidised to ferric salts :

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

Iodine is liberated from potassium iodide :

$$2KMnO_4 + 10KI + 8H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O.$$

Oxalic acid is oxidised to carbon dioxide :

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

Oxygen is liberated from hydrogen peroxide :

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O.$$

Potassium permanganate reacts with strong hydrochloric acid giving off Cl_2 :

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O.$$

(ii) **In alkaline solution.**— In alkaline solution 2 molecules of potassium permanganate give 3 atoms of available oxygen :

$$2KMnO_4 + H_2O = 2KOH + 2MnO_2 + 3O.$$

Alkaline potassium permanganate oxidises potassium iodide to iodate :

$$2KMnO_4 + H_2O + KI = 2MnO_2 + 2KOH + KIO_3.$$

Uses of potassium permanganate: (i) as an oxidising agent, (ii) as a disinfectant, (iii) in volumetric analysis, such as estimation of iron, oxalic acid, hydrogen peroxide, etc.

Detection and estimation.—(i) *Borax bead test.*—The colour of the bead is *purple* in oxidising flame, and *colourless* in reducing flame.

(ii) A *green* melt of manganate is formed by fusing a manganese compound with a mixture of caustic soda and potassium nitrate. The mass is extracted with water and acidified with acetic acid when a *pink* colour of permanganic acid develops.

(iii) A pink colour develops on adding dilute HNO_3 and lead dioxide to a solution of manganous salt, and warming :

$$2MnSO_4 + 5PbO_2 + 6HNO_3 = 2HMnO_4 + 2Pb(NO_3)_2 + 2H_2O.$$

(iv) A pink colour appears when a manganous salt is oxidised in cold dilute HNO_3 by sodium bismuthate—the reaction is quantitative.

$$2Mn(NO_3)_2 + 5NaBiO_3 + 16HNO_3 = 2HMnO_4 + 5NaNO_3 + 5Bi(NO_3)_3 + 7H_2O.$$

(v) In neutral solution in presence of zinc oxide potassium permanganate oxidises a hot solution of a manganous salt into MnO_2—the reaction is used for estimating manganese **(Volhard's method).**

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$$

Exercises

1. Describe the preparation of potassium dichromate from chrome iron-stone. Explain its action as an oxidising agent. From potassium dichromate how would you prepare (a) metallic chromium, (b) chromous chloride, (c) chrome alum, (d) chromyl chloride? *Bombay* 53.

2. Starting from pyrolusite how would you prepare (a) pure manganous chloride, (b) potassium permanganate? Explain the action of potassium permanganate as oxidising agent.

3. Explain what happens when : (a) chlorine is passed into a heated mixture of chromic oxide and coke. (b) sulphur dioxide is led into potassium dichromate solution acidified with sulphuric acid. (c) concentrated HCl is added to a solution of potassium dichromate, containing granulated zinc. (d) KI is added to potassium dichromate solution acidified with conc. HCl. (e) common salt is distilled with potassium dichromate and sulphuric acid. (f) potassium permanganate is added to a hot solution of oxalic acid acidified with sulphuric acid. (g) H_2O_2 is added to an acidified solution of ferrous sulphate. (i) potassium dichromate solution is treated with hydrogen peroxide.

Explain how the equivalent weights of $KMnO_4$ and $K_2Cr_2O_7$ are calculated.

4. How is potassium permanganate made from pyrolusite? Describe its action on ferrous sulphate. oxalic acid, hydrochloric acid, hydrogen peroxide and potassium iodide. *Punjab* '51.

XXXV

The inert gases

Helium, neon, argon, krypton, xenon and radon are known as the *inert gases*, because of their chemical inertness. All the inert gases except the radioactive radiation radon occur in the atmosphere. Though in traces only,—their relative abundance in the atmosphere in percentage by volume is helium 0.00052 ; neon 0·0015 ; argon 0·9323 ; krypton , 0·0001 ; xenon 0·000009 and hence their name the *rare gases of the atmosphere*.

History of the discovery.—The discovery of the rare gases of the atmosphere was due to an observation by Lord Rayleigh in 1892 that the atmospheric nitrogen was about 0·5% heavier than the nitrogen prepared chemically by heating ammonium nitrite or by reducing the oxides of nitrogen with heated iron —normal density: (a) *'chemical' nitrogen* = 1·2505, (b) *atmospheric nitrogen* = 1·2572. The difference was too great to be attributed to experimental errors, and it was suspected to be due to the presence of some *heavier* gas in the atmospheric nitrogen. Hence to account for this discrepancy, experiments were jointly undertaken by Lord Raleigh and Sir William Ramsay in order to isolate the heavier gas, if any, in the atmospheric nitrogen. Two methods were employed:

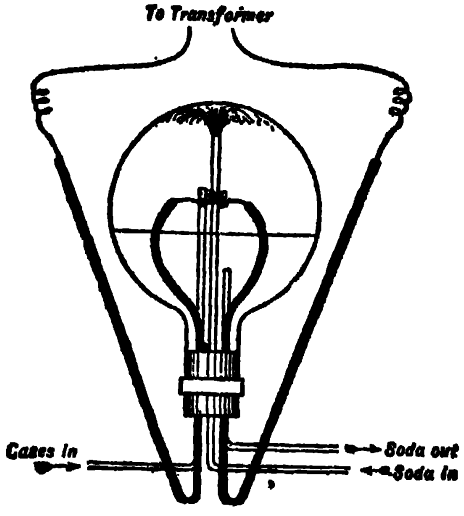


Fig. 192

(i) Rayleigh himself repeated the experiment of Cavendish who noticed as early as 1785 that a little residual gas (about 1/120 of the original volume) was left on sparking a mixture of air and oxygen over caustic potash and confirmed Cavendish's result—the residual gas did not give the spectrum of nitrogen. This residual gas was prepared in quantity and for this a mixture of air (9 vols.) and oxygen (11 vols.) was sparked between platinum electrodes in a large glass globe over caustic soda solution— the excess oxygen was absorbed by alkaline pyrogallate and the residual gas collected (fig. 192).

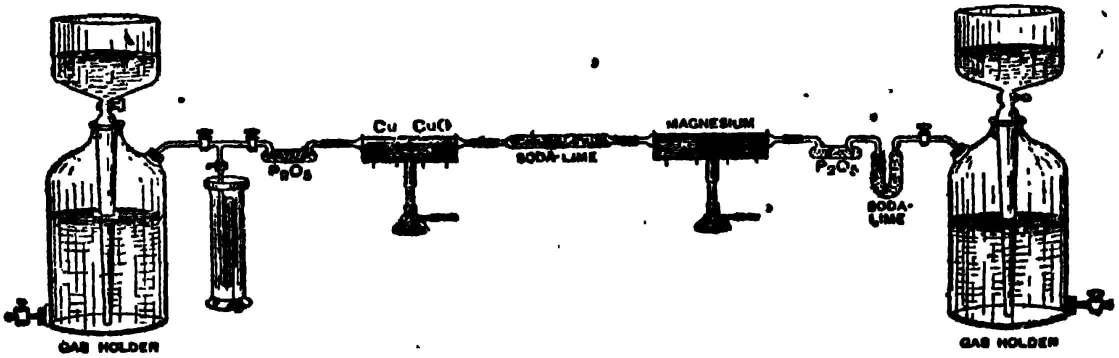


Fig. 193

(ii) At the suggestion of Ramsay the oxygen of air was absorbed by heated copper, and the nitrogen was then *repeatedly passed* (fig. 193) over heated magnesium which absorbed nitrogen as magnesium nitride, till there was left a little residual gas (1/80 of the original volume) with a density of 19·94 (H = 1). The spectrum of this gas, as also that of the residue obtained by Cavendish's method, differed from that of nitrogen or of any known gas. Hence it was taken to be a new element and one of the normal constituents of the atmosphere. It was called **argon** (meaning lazy or inactive), because of its reluctance to form chemical compounds.

An attempt to obtain argon from the uranium mineral **clevite** resulted in the discovery of *helium*, another normal constituent of the atmosphere, by Ramsay—the mineral on heating with the dilute sulphuric acid or in a vacuum evolved a gas containing about 20% nitrogen. The residual gas, left after the removal of nitrogen, was separated by fractional diffusion into argon and a new gas which gave the spectrum of helium which was discovered by Lockyer in the sun's atmosphere during a total eclipse in 1868. It was in 1895 that helium was discovered by Ramsay from terrestrial sources. Helium is inert chemically as argon.

The consideration of the position of argon and helium in the periodic table suggested that a whole family of inert gases might exist. Ramsay and Travers (1898), therefore, began systematic examination of the residual atmospheric gas.

The gas was partially liquefied by compression and cooling to—185° in liquid air and separated into gaseous and liquid fractions by rapid exhaustion. The gaseous fraction was cooled to—240° in liquid hydrogen when a portion solidified, the remaining gas was helium—the solid was found to be a new element, called *neon*. The liquid fraction on fractional distillation gave argon first, *krypton* next and *xenon* last. The investigation of the residues from the evaporation of 120 tons of liquid air failed to indicate the presence of any other gases.

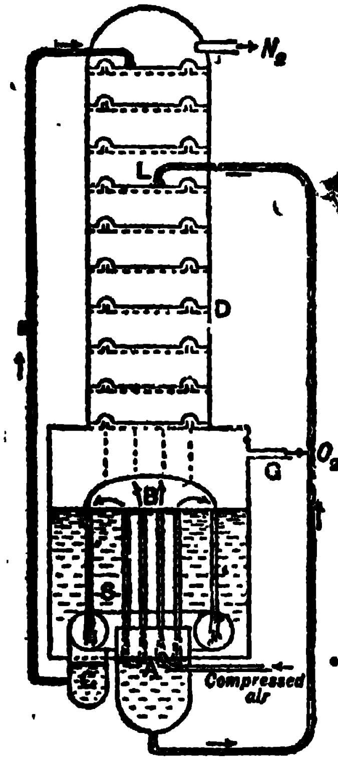


Fig. 194

Position in the Periodic Table.— It is quite in conformity with the rule of valency that the inert gases which form a family of no-valency elements have been placed in the zero-group (p. 169).

Atomic weight.— The atomic weight of the inert gases cannot be determined by chemical means. The ratio of the specific heat at constant pressure to that at constant volume for the inert gases is 1·66, showing the monatomic nature of the gases, i.e., their molecules consist of one atom only. Hence the atomic weight of an inert gas is equal to twice the relative density (H=1)—the latter being determined experimentally.

Inert gases from liquid air.— Air may be liquefied in Linde machine (p. 177) (cooling is due to expansion of air against molecular attraction, i.e., due to Joule-Thompson effect) or in Claude machine (cooling is due to external work done by the expanding air in an engine).

Compressed air at about 40 atmospheres is cooled by doing external work by expansion in an engine, when it partly liquefies and enters the bottom of Claude's rectifying column (fig. 194) and rises up a set of vertical pipes immersed in a bath of liquid oxygen, and gets liquefied—liquid rich in nitrogen collects in a pot C and is led to the top of the column and liquid rich in oxygen drains in A and is taken to a lower compartment L. On rectification nitrogen passes at the top of the column and liquid oxygen collects in the bath S—oxygen gas passes out at G. The cold of nitrogen and oxygen is utilised in heat interchanges. The gases are stored under pressure in steel cylinders.

The inert gases are produced commercially by the fractionation of liquid air. The boiling points of the various constituents of liquid air in degrees absolute are: helium 4°, neon 27°, nitrogen 77°, argon 87°, oxygen 90°, krypton 122° and xenon 164°. During the fractionation of liquid air gaseous helium and neon collect above liquid nitrogen in the pot C. The mixture of helium and neon is passed over heated calcium carbide to absorb the accompanying nitrogen and then cooled in liquid hydrogen when neon liquefies and helium passes out.

Argon collects in liquid oxygen and is separated from the latter by fractionation in a rectifying column provided with a coil of liquid nitrogen—argon, being more volatile, passes out as a gas; the liquid oxygen fraction contains the less volatile krypton and xenon which are fractionated.

Helium.—It occurs in the occluded state in all radio-active minerals. Natural gases from petroleum wells in U.S.A. and Canada contain as much as 1% by volume of helium. It is produced from this source by compression and cooling when all other gases condense. The thorium mineral *monazite sand*, found in Travancore in India, contains about 1 c.c. of helium per gram. Being non-inflammable and having a lifting power of about 92% of that of hydrogen it is used for filling airships and balloons. Helium is present in the Sun's atmosphere.

Neon.—It is produced commercially from liquid air. It finds use in filling neon-lamps (giving red light) used extensively as advertising signs.

Argon.—Argon is obtained from liquid air. It was formerly made by passing dry air over a mixture of 90 parts of calcium carbide and 10 parts of calcium chloride, heated to 800° in iron retorts—the nitrogen and oxygen are absorbed as calcium cyanamide and carbonate respectively. $CaC_2+N_2 = NCaCN+C$. The residual gas is then passed over heated copper oxide to oxidise carbon monoxide to the dioxide and then through potash to absorb the carbon dioxide and finally dried.

Argon is used for filling metal filament electric lamps, and for creating an inert atmosphere in arc-welding.

Inert gases are used now-a-days in *fluorescent lighting tubes*.

Exercises

(1) What led to the discovery of the inert gases and how were they isolated? Discuss their position in the periodic table.

(2) How is argon obtained from air? Describe its properties and uses. How is its atomic weight determined?

XXVI

Chemical calculations

On density and specific gravity.—The *density* (*absolute density*) of a substance is its mass per unit volume, $d = m/v$,

where m is the mass, v the volume and d the density of a body.

The unit of volume in *C.G.S.* system is 1 c.c.; hence the mass in grams, of 1 c.c. of a substance is its density; e.g., 'the density of diamond is 3·52' means that the mass of 1 cubic centimetre of diamond is 3·52 grams.

The *normal* density of a gas is the mass in grams of one litre of the gas measured at N.T.P.

The normal density of hydrogen is 0·0899 gram.

The *relative* density of a substance is the ratio of its density to the density of a standard substance *under identical conditions* of temperature and pressure.

In the case of *gases and vapours* the standard substance is generally *hydrogen* and occasionally *air or oxygen*. The relative density is often called the *vapour density* (p. 85). The vapour density may be converted from one standard to another in the following way:

$$\text{Vapour density } (H = 1) = \frac{\text{density of the gas}}{\text{density of hydrogen}}$$

$$= \frac{\text{density of the gas}}{\text{density of oxygen}} \times \frac{\text{density of oxygen}}{\text{density of hydrogen}}$$

$$\therefore \text{ density of a gas } (H = 1) = \text{density of the gas } (O = 1) \times \text{density of oxygen } (H = 1).$$

$$\text{Also, density of a gas } (H = 1) = \text{density of the gas } (\text{air} = 1) \times \text{density of air } (H = 1).$$

As already stated (p. 86),

(a) $$\text{the density of a gas } (H = 1) = \frac{\text{wt. of 1 litre of gas at N.T.P.}}{0{\cdot}09 \text{ gm}}$$

$\therefore$ wt. of 1 litre of a gas at N.T.P. = its density (H = 1) × 0·09 gm.

$\therefore$ wt. of 1 litre of air at N.T.P. = 14·4 × 0·09 gm = 1·296 gm, since the density of air (H=1) is 14·4.

(b) *Gram molar volume of a gas is 22·4 litres at N.T.P.* i.e., *gram molecular weight of a gas occupies 22·4 litres at N.T.P.*

In the case of *liquids and solids*, the standard substance is *water* at 4°C; the relative density is then called the *specific gravity*.

In *C. G. S.* system, the absolute density of water at 4°C is unity. Hence the *specific gravity of a substance is numerically equal to its density*; e.g., the absolute density of mercury is 13·6, the figure 13·6 also indicates its specific gravity.

Percentage.—By percent is meant parts in 100 parts. In the case of *solids*, percentage always refers to *weight*; e.g., "a mineral of copper contains 2·5 per cent copper" means that 100 parts by weight of the mineral contain 2·5 parts by weight of copper.

In the case of *solutions*, percentage refers either (i) to the weight of a substance *per 100 parts by weight of the solution*, or (ii) to the weight in grams of a substance *per 100 c.c. of the solution*; e.g., "a 20 per cent sulphuric acid" may either mean (i) 20 gms. of sulphuric acid per 100 gms. of the solution, or (ii) 20 gms. of sulphuric acid per 100 c.c. of the solution. The context alone will decide which meaning is applicable.

In the case of *gases*, percentage generally refers to *volume*, unless otherwise stated.

Exercises

(1) Calculate the weight of 10 litres of carbon dioxide measured at 0°C and 722 mm. pressure.

The molecular weight of CO_2 is 44, and its density (H=1) is 22.

Let the volume of CO_2 at N.T.P. = v litres.

$\therefore$ $v \times 760/273 = 10 \times 722/273$, whence v=9·5 litres.

The problem may be worked out by either of the two methods:

(a) The molar volume of a gas is 22·4 litres at N.T.P.

∴ 22·4 litres of carbon dioxide at N.T.P. weigh 44 gms.

∴ 9·5 litres of CO_2 at N.T.P. weigh 44×9·5/22·4=18·66 gms.

(b) 1 litre of hydrogen at N.T.P. weighs 0·089 gm.

∴ 1 litre of CO_2 at N.T.P. weighs (0·089×22) gm.

∴ 9·5 litres of CO_2 at N.T.P. weigh (0·089×22×9·5) or 18·60 gms.

(2) Calculate the volume occupied by 6·4 gms. of sulphur dioxide measured : (i) at N.T.P., (ii) at 273°C and 950 mm. pressure.

The molecular weight of SO_2 is 64, and hence the density (H=1) is 32.

(a) 64 gms. of SO_2 occupy 22·4 litres at N.T.P.

∴ 6·4 gms. of SO_2 occupy 2·24 litres at N.T.P.

(b) 0·089 gm. of hydrogen occupy 1 litre at N.T.P.

∴ 0·089×32 gm. of SO_2 occupy 1 litre at N.T.P.

∴ 6·4 gm. of SO_2 occupy 6·4/0·089×32, i.e., approximately 2·24 litres at N.T.P.

Let the volume at 273°C and 950 mm. be v litres.

∴ v×950/546=2·24×760/273, whence v=1·792 litres.

(3) 500 c.c. of a gas at 27°C and 750 mm. pressure weight 0·6414 gm. Calculate its (a) normal density, (b) relative density (H=1), (c) relative density (air=1).

Let the volume of the gas at N.T.P. = v c.c.

∴ v×760/273 = 500×750/300, whence v = 449 c.c. = 0·449 litre.

(a) 0·449 litre at N.T.P. weighs 0·6414 gm.

∴ 1 litre at N.T.P. weighs 0·6414/0·449 or 1·43 gm.

∴ normal density of the gas = 1·43 gm.

(b) $$\text{Density (H=1)} = \frac{\text{normal density of the gas}}{\text{nomal density of } H_2} = \frac{1·43}{0·089} = 16.$$

(c) Density of the gas (H=1) = its density (air=1)×density of air (H=1)

The density of air (H=1) is 14·4

∴ 16 = density (air=1)×14·4, ∴ density (air=1) = 16/14·4 = 1·11

$$\text{or density (air=1)} = \frac{\text{normal density of the gas}}{\text{normal density of air}} = \frac{1·43}{1·293} = 1·11$$

1 litre of air at N.T.P. weighs 1·293 gm, i.e., normal density of air is 1·293 gm.

(4) A sample of gas weighing 0·1100 gm. occupies a volume of 24 c.c. at 27°C and 740 mm. pressure. Calculate the molecular weight of the gas.

Let the volume of the gas at N.T.P. = v c.c.

∴ v×760/273 = 24×740/300, whence v = 21·26 c.c.

Molar volume of a gas = 22400 c.c. at N.T.P.

21·26 c.c. of the gas weigh 0·11 gm.

∴ 22400 c.c. of the gas weigh 0·11×22400/21·26 or 115·9 gm.

∴ gram molecular weight of the gas = 115·9 gm.

(5) Determine the density of air (H=1), supposing it to be a mixture of 4 volumes of nitrogen and one volume of oxygen. Given the densities (H=1) of oxygen and nitrogen are, respectively, 16 and 14.

Weight of 100 volumes of air = weight of 80 volumes of nitrogen.
+ weight of 20 volumes of oxygen.

∴ 100×density of air = 80×14 + 20×16, or density of air = 14·4.

(6) How much pure nitric acid is present in a litre of a sample of nitric acid (sp. gr. 1·42)? The percentage strength of the acid is 70.

1 c.c. of the sample of the acid weighs 1·42 gms.

∴ 1 litre ,, ,, ,, ,, ,, 1420 gms.

The percentage strength refers to weight.

100 gms. of the sample contain 70 gms. of pure nitric acid.

∴ 1420 gm. contain (1420×0·70) or 994 gm. of real nitric acid.

∴ 994 gms. of pure nitric acid are present in a litre.

(7) 50 gms. of a one-pound sample of clay is rejected by repeated sedimentation, as worthless for pottery. Calculate the requirement of raw clay of a pottery works, consuming 1000 tons of pure clay annually.

1 ton = 2240 lbs.; 1 lb. = 453·6 gm.

1 lb. of raw clay contains 50 gms. or 0·11 lb. of rejection.

i.e., 1 lb. of raw clay contains 0·89 lb. of pure clay.

∴ 1000 tons of pure clay are present in (1000×2240)/0·89 lbs. of raw clay.

∴ the annual requirement = 1000×2240/0·89 lbs. of raw clay.

∴ the annual requirement = 1000/0·89 = 1121·35 tons of raw clay.

---

8. Find the weight of 6·229 litres of oxygen (density 16) measured at 27°C and 750 mm. pressure. Normal density of hydrogen is 0·089 gm. 7·968 gm.

9. 2·257 litres of a gas at 27°C and 740 mm. weigh 2·857 gm. Find its density. Normal density of hydrogen is 0·089 gm.
Normal density = 1·428 gm. Density (H=1) = 16.

10. The density of carbon dioxide relative to air is 1·528. Find its density relative to hydrogen. 22.

11. Calculate the volume occupied by 1·7 gms. of ammonia: (i) at N.T.P., (ii) at 27°C and 740 mm. pressure. (i) 2·24*l*. (ii) 2·527*l*.

12. A sample of gas weighing 0·8 gm. occupies 1247 c.c. at 27°C and 750 mm. Calculate the molecular weight of the gas. 16

13. A flask weighs 130 gm. when full of air and 129·84 gm. when some air has been pumped out. When opened under water, 125 c.c. of water enter. Find the weight of 1 litre of air. 1·28 gm.

14. The normal density of a sample of impure hydrogen sulphide is found to be 1·4628. If hydrogen alone be present as an impurity, calculate the percentage of hydrogen by volume. Given that the densities of hydrogen and its sulphide are respectively 0·09 and 1·52 gm. per litre. 4 per cent.

15. One hundred tons of a mineral containing 59% carnallite pass through a refinery and are made to yield potassium chloride. If the recovery is 70 per cent, calculate the amount of potassium chloride obtained from 1000 tons of the mineral. Carnallite contains 26·85% potassium chloride. 110·9 tons.

16. The amount of fuel consumption per barrel (376 lbs.) of cement produced is 120 lbs. of ash-free coal. How many tons of coal must be provided for a furnace producing 200 tons of cement per day—the sample of coal containing 10 per cent ash. 70·92 tons.

17. One litre of a solution of sodium carbonate contained 5·20 gms. of the solid and 105·2 gm. of the same solution occupied 100 c.c. Find the percentage strength (per 100 gm.) of the solution. 0·4943%.

18. A litre of sea water (sp. gr. 1·03) is evaporated to dryness and found to give as residue 36·4 gms. of salt; find the percentage of solid matter per 100 gms. of sea water. 3·534%

19. A sample of sulphuric acid contains 31·6 gm. of pure acid per 100 gm. of the acid solution and its specific gravity is 1·26. Calculate the weight of real acid in every 100 c.c. of the solution. 39·8 gm.

20. Calculate weight of pure HNO_3 in 10 c.c. of commercial nitric acid (sp. gr. 1·4) containing 65% HNO_3 by weight. 9·1 gm.

On percentage composition.—(i) Composition from formula.— The percentage composition of a compound states the weight of each constituent in 100 parts by weight of the substance. In order to determine it:

(a) find the molecular weight (i.e., the sum of the atomic weights of all the constituent atoms) of a compound, represented by its formula, and then :

(b) divide the total weight of each constituent by the molecular weight and multiply by 100.

(i) Calculate the percentage composition of anhydrous sodium sulphate. Its molecular formula is Na_2SO_4 :

wt. of 2 atoms of sodium = 2 × 23 = 46
wt. of 1 atom of sulphur = 1 × 32 = 32
wt. of 4 atoms of oxygen = 4 × 16 = 64

∴ molecular weight of Na_2SO_4 = 46 + 32 + 64 = 142.

Now, 142 parts by wt. of Na_2SO_4 contain 46 parts by wt. of sodium.
∴ 100 ,, ,, ,, ,, 46 × 100/142 or 32·4 ,, ,, ,,
∴ % of sodium = 32·40.

Similarly, % of sulphur = 32 × 100/142 = 22·53; % of oxygen = 45·07.

(ii) Calculate the percentage of iron, NH_4 and SO_4 groups, and water in ferric ammonium sulphate of the formula, $(NH_4)_2SO_4,Fe_2(SO_4)_3,24H_2O$.

Molecular weight from formula :

wt. of 2 atoms of Fe = 2 × 56 = 112·0
wt. of 3 SO_4—groups = 3 × 96 = 228·0
wt. of 2 NH_4— ,, = 2 × 18 = 36·9
wt. of 1 SO_4— ,, = 1 × 96 = 96·0
wt. of 24 H_2O ,, = 24 × 18 = 432·0

Total = 964·0

In 964 gm. of the compound there are 112 gms. of iron.
∴ in 100 ,, ,, ,, ,, 112 × 100/964 or 11·62 gms. of iron
∴ % of Fe = 11·62

Similarly, % of NH_4 = (36 × 100)/964 = 3·73
% of SO_4 = (4 × 96 × 100)/964 = 39·83
% of water = (432 × 100)/964 = 44·82.

(ii) Formula from percentage composition.— The formula of a compound is deduced by finding the number of atoms of each constituent element from its percentage composition.

Suppose the formula of a compound containing the elements A (at wt. a) and B (at. wt. b) is A_xB_y, where x and y are the number of atoms of A and B respectively.

$$\therefore \quad \%\text{ of A} = ax.\ 100/(ax+by), \text{ and } \%\text{ of B} = by.\ 100/(ax+by).$$

$$\frac{\%\text{ of A}}{\%\text{ of B}} = \frac{ax}{by} \text{ or } \frac{\%\text{ of A}}{a} : \frac{\%\text{ of B}}{b} = x:y$$

i.e., $\dfrac{\%\text{ of A}}{\text{at. wt. of A}} : \dfrac{\%\text{ of B}}{\text{at wt. of B}}$ = number of atom of A: number of atom of B.

***i.e.* the quotient of the percentage of each element divided by its atomic weight is a number which is proportional to the number of atoms in the compound.**

Hence to deduce the formula from percentage composition:

(i) divide the percentage of each element by its atomic weight to obtain the ratio of number of atoms of each element;

(ii) divide each number as obtained in (i), by the smallest of them and then multiply the quotients, if necessary, by a small number, in order to express the ratio in the simple whole numbers, since fractional atoms are inadmissible.

The formula of a compound directly deduced from its percentage composition is called the **simplest** or **empirical formula.** It simply shows the relative number of atoms of each element present in the compound.

The **molecular formula,** on the other hand, gives the *exact* number of atoms of each element in a molecule. Hence the molecular formula is either equal to or some multiple of the empirical formula. Let the empirical formula of a compound be $\mathrm{A}p\mathrm{B}q$ then:

$$(\mathrm{A}p\mathrm{B}q)_n = \text{molecular formula.}$$

$$\text{or } (ap+bq)n = \text{molecular weight} = 2 \times \text{vapour density } (\mathrm{H}=1).$$

$$\therefore\ n = \frac{2 \times \text{vapour density}}{ap+bq}\text{, where } a, b \text{ are the atomic weights and}$$

p and q are the atoms of A and B respectively in the empirical formula $\mathrm{A}p\mathrm{B}q$, and n is a simple integer.

Exercises

1. A compound of C, H and O contains C = 40% H = 6·67%. Its molecular ight is 180. Find its formula. *Calcutta* '38.

C = 40%, H = 6·67% ∴ O = 100 − (40 + 6·67) = 53·33%.

Dividing the percentage of each element by its atomic weight

C = 40/12 = 3·33, H = 6·67/1 = 6·67, O = 53·33/16 = 3·33.

These numbers are proportional to the number of atoms of the elements present in one molecule of the compound.

Dividing the numbers by the lowest number to transform them into whole numbers, since fractional atoms are inadmissible.

C = 3·33/3·33 = 1, H = 6·67/3·33 = 2. O = 3·33/3·33 = 1

∴ the simplest formula is CH_2O and the molecular formula is $(CH_2O)n$. Now, the molecular weight is 180.

∴ $(CH_2O)n = 180$, or $(12+2+16)n = 180$, whence n = 6.

Hence the molecular formula is $(CH_2O)_6$ or $C_6H_{12}O_6$.

2. A compound containing Na, S, O and H gave on analysis the following result: Na = 14·31% S = 9·97% H = 6·25% O = 69·47%. Calculate the formula on the assumption that all the hydrogen in the compound is present in combination with oxygen as water. *Calcutta* '18.

Dividing by atomic weights: Na = 14·31/23 = 0·62, S = 9·97/32 = 0·31,
H = 6·25/1 = 6·25, O = 69·47/16 = 4·24.

Dividing the quotients by the lowest number:

Na = 0·62/0·31 = 2, S = 0·31/0·31 = 1,
H = 6·25/0·31 = 20, O = 4·34/0·31 = 14.

Hence the formula is $Na_2SH_{20}O_{14}$. But all the hydrogen is present in combination with oxygen as water, 20 atoms of hydrogen combine with 10 atoms of oxygen to form $10H_2O$. Hence the formula is $Na_2SO_4, 10H_2O$.

3. Two oxides of a metal contain 27·6 and 30% oxygen respectively. If formula of the first oxide be M_3O_4, find that of the second. *Cal.* '40.

Let *a* be the atomic weight of the metal M. The first oxide contain 27·6% oxygen, and (100−27·6) or 72·4% of the metal.

$$\frac{\%\text{ of M}}{\text{at. wt. of M}} \bigg/ \frac{\%\text{ of }O_2}{\text{at. wt.. of }O_2} = \frac{\text{No. of atoms of M}}{\text{No.. of atoms of }O_2}$$

or $72{\cdot}4/a : 27{\cdot}6/16 = 3:4$; whence $a = 55{\cdot}97$.

The second oxide contains 30% O_2 and 70% M..

$$\frac{\text{No. of atoms of M}}{\text{No. of atoms of }O_2} = \frac{70}{55{\cdot}97} \bigg/ \frac{30}{16} = \frac{1{\cdot}25}{1{\cdot}87} = \frac{1}{1{\cdot}5} = \frac{2}{3}$$

since atoms cannot be divided : $\therefore$ the formula of the oxide is M_2O_3.

4. Calculate the percentage of P_2O_5 in $Na_2HPO_4, 12H_2O$. *Cal.* '10.

Mol. wt. of $Na_2HPO_4, 12H_2O = 358$. Mol. wt. of $P_2O_5 = 142$.

$2Na_2HPO_4, 12H_2O = Na_4P_2O_7(2Na_2O, P_2O_5) + 25H_2O$ by heat.

$\therefore$ 2×358 or 716 gms. of the phosphate crystals contain 142 gms. of P_2O_5

$\therefore$ % of phosphoric anhydride, $P_2O_5 = 142 \times 100/716 = 19{\cdot}83$.

5. One gram of phosphorus gave 2·29 gm. of an oxdie on burning. Find out its simple formula.

The wt. of O_2 combining with phosphorus $= 2{\cdot}29 - 1 = 1{\cdot}29$.

Let the formula of the oxide be $PxOy$, where x and y are the atoms of P and O_2 respectively, then in the formula-weight of the oxide :

wt. of phosphorus : wt. of oxygen $= 31x : 16y$.

i.e., wt. of P : wt. of O_2 = at. wt. of P×x : at. wt. of O_2×y.

$$\text{or } \frac{\text{wt. of P}}{\text{at. wt. of P}} : \frac{\text{wt. of }O_2}{\text{at. wt. }O_2} = x:y. = \frac{1}{31} : \frac{1{\cdot}29}{16} = x:y$$

i.e., $x : y = 0{\cdot}032 : 0{\cdot}080$. Dividing by the smallest number, $x : y = 1 : 2{\cdot}5$.

Multiplying by 2, $x : y = 2 : 5$. Hence the formula is P_2O_5.

6. Find the formula from the following percentage composition :

$MgO = 23{\cdot}48\%$; $FeO = 41{\cdot}74\%$; $SiO_2 = 34{\cdot}78\%$.

Dividing the % of each of these compounds by respective mol. wts.

$$MgO = \frac{23{\cdot}48}{40} = 0{\cdot}587;\quad FeO = \frac{41{\cdot}74}{72} = 0{\cdot}58;\quad SiO_2 = \frac{34{\cdot}78}{60} = 0{\cdot}579.$$

Dividing each by 0·58, $MgO = 1$; $FeO = 1$: $SiO_2 = 1$.

Hence the simplest formula is MgO,FeO,SiO_2, or $MgFeSiO_4$.

Assume the following atomic weights : K = 39·1, Cl = 35·5, Mg = 24, H = 1, Al = 27, Na = 23, Pb = 207, Cu = 63·5, P = 31, K = 39·1.

7. Determine the percentage composition of : (*a*) potassium chlorate, (*b*) Epsom salt ($MgSO_4, 7H_2O$), (*c*) cryolite ($AlF_3, 3NaF$)

(*a*) K 31·89; Cl 28·95; O 39·16; (*b*) Mg 9·76; S 13·01; O 26·01; H_2O 51·22; (*c*) Na 32·86; Al 12·86; F 54·28

8. Calculate the percentage of—(*a*) lead in white lead ($2PbCO_3, Pb(OH)_2$), (*b*) chlorine in carnallite ($KCl, MgCl_2, 6H_2O$), (*c*) nitric anhydride (N_2O_5) in potassium nitrate, (*d*) water of crystallisation in blue vitriol, (*e*) carbon dioxide in calcium carbonate. (a) 80·13; (b) 38·36; (c) 53·40; (d) 36·07; (e) 44.

9. A mixture of cuprous and cupric oxide was found to contain 88% Cu. Calculate the proportion of the two compounds in the mixture, taking the atomic weight of copper to be 64. Cu_2O, 90%; CuO, 10%. *Nagpur* '32.

10. Water contains 11·11% hydrogen and 88·88% oxygen. Calculate its formula.
H_2O

11. A compound of C, H and O contains 42·105% carbon, 6·432% hydrogen and the rest oxygen. Its molecular weight is 342. Calculate the formula.
$C_{12}H_{22}O_{11}$

12. A compound contains 82·74% carbon and 17·26% hydrogen. Its vapour density is 29. Find the formula.
C_4H_{10}

13. A crystalline salt contains 18·55% sodium, 25·81% sulphur, 19·35% oxygen (which is not present as water) and 36·29% water of crystallisation. What is its formula?
$Na_2S_2O_3.5H_2O$.

14. 12·325 gm. of Epsom salt lose 6·306 gms. of water on dehydration and leave behind $MgSO_4$. Calculate the formula of Epsom salt.
Banaras '27. $MgSO_4, 7H_2O$.

15. A compound was found on analysis to have the following composition: K = 17·8; Ni = 13·5, SO_4 = 44, H_2O = 24·7%. What is its formula? Ni = 58·7.
Bombay '18. K_2SO_4, $NiSO_4$, $6H_2O$.

16. A substance gives on analysis the following results:

Na – 13·4%; Sb – 23·3%; S – 24·9% and H_2O – 38·4%.

It contains 7% hygroscopic moisture. Calculate the formula of the compound. (Na = 23, Sb = 120, S = 32).
Calcutta '25. Na_3SbS_4, $9H_2O$.

17. Work out the formula of a mineral from the following percentage composition: CaO 48; P_2O_5 41·3; and $CaCl_2$ 10·7.
$3Ca_3(PO_4)_2,CaCl_2$.

18. Calculate the molecular formula from the results of analysis given: S – 23·7%, Cl – 52·6% and the rest being oxygen. Vapour density = 67·5.
SO_2Cl_2.

19. A substance has the following percentage composition: N – 35, H – 5, O – 60. On being heated it yields a gas containing N 63·63% and O 36·37%. Calculate the formula of each substance. Name the original substance and construct the equation representing the chemical change. *Andhra University.*
NH_4NO_3, N_2O; $NH_4NO_3 = N_2O + 2H_2O$.

20. Express the percentage composition of crystallised sodium carbonate, Na_2CO_3, $10H_2O$, in terms of: (a) anhydrous sodium carbonate and water of crystallisation, and (b) Na_2O. Calculate the percentage of Na_2O in anhydrous sodium carbonate.
(a) H_2O 62·94; Na_2CO_3 37·06; (b) 21·68; 58·49.

21. The percentage composition of chloride of silicon has been ascertained to be Si = 16·47%, Cl = 83·53%. Its vapour density is 85 (H = 1). Calculate the atomic weight of silicon.
28·0.

22. 10 gm. of a substance when strongly heated gave 2·55 gm. of carbon dioxide and 0·525 gm. of water and left a residue of copper oxide. What is its simplest formula?
$2CuCO_3$, $Cu(OH)_2$.

23. 6·29 gm. of crystallised aluminium sulphate lost 3·06 gm. of water on heating. 2·59 gm. of the crystals with $BaCl_2$ gave 2·72 gm. of $BaSO_4$. Calculate the formula of the crystals. Ba = 137.
$Al_2(SO_4)_3,18H_2O$.

24. A crystallised salt on being rendered anhydrous loses 45·6% of the weight. The anhydrous salt has the percentage composition: Al = 10·5, K = 15·1, S = 24·8. O = 49·6. Calculate the simplest formula of the anhydrous and the crystallised salt.
Allahabad '08. $KAlS_2O_8$, and $KAlS_2O_8$, $12H_2O$.

25. Carbon monoxide was passed over heated copper oxide which lost 0·413 gm. and produced 1·137 gm. of CO_2. Find the formula of carbon monoxide.
Punjab '44. CO.

26. An element X, forms a hydride containing 25 per cent of hydrogen; X also forms two oxides A and B, containing 57·1 and 72·7 per cent of oxygen respectively. The atomic weight of the element is 12. Find the formula of the hydride and the two oxides.
XH_4; XO, and XO_2.

27. 0·15 gm. of an organic substance containing C,H,O and N on being heated with excess of copper oxide gave 0·09 gm. water, 0·11 gm. CO_2, and 56 c.c. nitrogen at N.T.P. Find its formula. CON_2H_4.

28. A monobasic organic acid contains 6·66% H, 39·96% C and the rest oxygen: 0·167 gm. of the silver salt of the acid gave 0·108 gm. of silver on ignition. Find the formula of the acid. Ag = 108. $C_2H_4O_2$.

29. The vapour density of the hydride of an element is 17. Its binary compound with silver contains 87·10% of the latter. Ag = 108. Find the at. wt. of the element. 32.

30. An element forms three chlorides containing 59·67, 68·93, and 74·73 per cent of chlorine. The vapour density of the highest chloride is 95. Deduce the valencies of the element. 2, 3, and 4.

31. 0·21 g. of a gaseous hydrocarbon on combustion gave 0·66 g. of CO_2 and 0·27 g. of H_2O; 304 c.c. of the hydrocarbon at 27°C and 750 mm. weighed 0·344 gm. Find the formula. *Punjab* '46. C_3H_6.

32. 0·245 gm. of an inorganic acid having the percentage composition of H 2·04, S 32·65, and O 65·3, neutralises 0·20 gm. of caustic soda. Calculate the formula of the acid, and its basicity. H_2SO_4; basicity 2.

On chemical equations.—A chemical equation has got a quantitative significance. It indicates the relative amounts by *weight* (also, by *volume* in the case of gases) of different substances involved in a chemical reaction. It may, therefore, be used in working out chemical problems. The following informations will be found useful in the chemical calculations:

(i) *All reactions represented by chemical equations are assumed to take place at N.T.P., i.e., at 0°C and 760 mm. pressure.*

(ii) *The weight of 1 litre of hydrogen at N.T.P.* = *0·0899 gm.*

Density of air (relative to hydrogen) is 14·4.

Weight of 1 litre of air at N.T.P. = 14·4 × 0·0899 = 1·295 gms.

(iii) *Molecular weight of a gas* = *2* × its vapour density (H = 1).

Vapour density of a gas (H = 1) = its vapour density (O = 1).
× vapour density of oxygen (H = 1).

(iv) *Mass* = *volume* × *density*

(v) *Atomic weight* = *Equivalent weight* × *valency*

(vi) PV/T = P′V′/T′ where P, V, T and P′, V′, T′ are the pressure, volume and temperature of a gas under two sets of conditions.

For *moist gases,* the barometric pressure (P) = pressure of the gas (p) + aqueous tension (f) at the temperature at which the gas is collected: ∴ $p = P - f$.

(vii) Atoms and molecules stand for gram-atoms and gram-molecules, i.e., atomic weight and molecular weight expressed in grams.

(viii) *In the synthesis of water from its elements, two-thirds the contraction* = *the volume of hydrogen, and one-third the contraction* = *the volume of oxygen.*

(ix) One gram molecule of a gas occupies 22·4 litres at N.T.P.

Exercises

(a) Gravimetric analysis.—*Calculations involving chemical equations, but not introducing gas volumes.*

(1) How much carbon is required to reduce 165 gms. of CO_2 to CO?

$$\underset{44}{CO_2} + \underset{12}{C} = 2CO$$

44 gm. CO_2 are reduced by 12 gm. carbon.

∴ 165 gm. CO_2 are reduced by 45 gm. carbon.

(2) What weight of chalk must be decomposed by HCl to yield sufficient CO_2 to convert 50 gm. of NaOH to sodium carbonate.

$$\underset{2\times 40}{2NaOH} + \underset{44}{CO_2} = Na_2CO_3 + H_2O.$$

80 gm. of NaOH react with 44 gm. of CO_2

∴ 50 gm. of NaOH react with 55/2 gm. of CO_2

$$\underset{100}{CaCO_3} + 2HCl = CaCl_2 + H_2O + \underset{44}{CO_2}$$

44 gm. of CO_2 are obtained from 100 gm. of $CaCO_3$

55/2 gm. of CO_2 are obtained from 62·5 gm. of $CaCO_3$

∴ weight of chalk required = 62·5 gm.

3. 8 gms. of pure manganese dioxide are heated with an excess of HCl and the gas evolved is passed into a solution of KI. Calculate the weight of iodine liberated. Molecular weight of $MnO_2 = 55+2\times16 = 87$. *Nagpur* '33.

$$\underset{87}{MnO_2} + 4HCl = MnCl_2 + 2H_2O + \underset{71}{Cl_2}; \quad 2KI + \underset{71}{Cl_2} = 2KCl + \underset{2\times 127}{I_2}$$

87 gms. of MnO_2 produce 71 gms. of chlorine

∴ 8 gms „ „ $71 \times 8/87$ or 6·528 gm. of chlorine.

35·5 gm. chlorine liberate 127 gm. of iodine

∴ 6·528 gm. „ „ $127 \times 6{\cdot}528/35{\cdot}5$ or 23·35 gm. of iodine

∴ the weight of iodine liberated = 23·35 gms.

4. How much potassium chlorate must be strongly heated to yield as much oxygen as would be obtained from 200 gms. of mercurric oxide? *Calcutta*, '46

Moleculer weight of $KClO_3$ = 122·5, and that of HgO = 216.

$$\underset{432}{2HgO} = 2Hg + \underset{32}{O_2}; \qquad \underset{245}{2KClO_3} = 2KCl + \underset{96}{3O_2}$$

432 gms. of HgO produce 32 gms. of oxygen.

∴ 200 gms. „ „ $32 \times 200/432$ or 14·8 gm. of oxygen.

96 gms. of oxygen are obtained from 245 gms. of $KClO_3$.

∴ 14·8 gms. „ „ „ „ $245 \times 14{\cdot}8/96$ or 37·78 gm. of $KClO_3$

∴ the amount og $KClO_3$ required = 37·78 gms.

5. 1·84 gms. of a mixture of $CaCO_3$ and $MgCO_3$ is strongly heated till no further loss of weight takes place. The residue weighs 0·96 gm. Calculate the percentage composition of the mixture. *U. P. Board* '43.

Let the weight of $CaCO_3$ = x gms., then the wt. of $MgCO_3$ = $(1{\cdot}84-x)$ gms.

$$\underset{100}{CaCO_3} = \underset{56}{CaO} + CO_2$$

i.e., 100 gms. of $CaCO_3$ leave a residue of 56 gms. of CaO.

∴ x gms. „ „ „ $56x/100$ gm. of CaO.

$$\underset{84}{MgCO_3} = \underset{40}{MgO} + CO_2$$

i.e., 84 gms. of $MgCO_3$ leave a residue of 40 gms. of MgO.

$\therefore$ $(1{\cdot}84-x)$ gms. leave a residue of $40(1{\cdot}84-x)/84$ gm. of MgO.

$$\therefore\ \frac{56x}{100}+\frac{40(1{\cdot}84-x)}{84}=0{\cdot}96,\ \text{whence } x=1.$$

$\therefore$ % of $CaCO_3=1\times100/1{\cdot}84=54{\cdot}35$; % of $MgCO_3=0{\cdot}84\times100/1{\cdot}84=45{\cdot}65$.

6. A sample of chalk contained as impurity a form of clay which lost 14·5 per cent of its weight on prolonged heating. 5 gms. of the chalk were heated and the total loss in weight (due to evolution of water and carbon dioxide) was 1·507 gm. Calculate the percentage of chalk in the sample.

Suppose 5 gm. of the sample contain x gm. of pure chalk; then amount of clay = $(5-x)$ gms. $\underset{100}{CaCO_3}=CaO+\underset{44}{CO_2}$

100 gms. of chalk lose 44 gm. on heating.

$\therefore$ x gms. „ „ „ $0{\cdot}44x$ gm.

100 gms. of clay lose 14·5 gms. on heating.

$\therefore$ $(5-x)$ gm. „ „ $0{\cdot}145\ (5-x)$ gm. on heating.

$\therefore$ $0{\cdot}44x+0{\cdot}145\ (5-x)=1{\cdot}507$, whence $x=2{\cdot}65$.

$\therefore$ the % of chalk in the sample$=2{\cdot}65\times100/5=53$.

7. 0·5 gm. of a mixture of KCl and KI dissolved in water and precipitated with silver nitrate gave 0·809 gm. of silver chloride and iodide mixture. Calculate the weight of KCl in the 0·5 gm. of the mixture.

Suppose the weight of KCl in the mixture is x gm.,

the weight of KI = $(0{\cdot}5-x)$ gm.

$$\underset{74\cdot5}{KCl}+AgNO_3=KNO_3+\underset{143\cdot5}{AgCl};\quad \underset{166}{KI}+AgNO_3=KNO_3+\underset{235}{AgI}$$

74·5 gms. of KCl produce 143·5 gms. of AgCl

x gm. „ „ „ $143{\cdot}5x/74{\cdot}5$ gm. of AgCl

166 gms. of KI produce 235 gms. of AgI.

$\therefore$ $(0{\cdot}5-x)$ gms. of KI produce $235\ (0{\cdot}5-x)/166$ gms. of AgI.

$$\therefore\ \frac{143{\cdot}5x}{74{\cdot}5}+\frac{235\ (0{\cdot}5-x)}{166}=0{\cdot}809,\ \text{whenece } x=0{\cdot}20.$$

(b) Calculations on equations involving gas volumes.

8. You are given a balloon with a capacity of 1000 litres and you are to it with hydrogen at 30°C and ~~550~~ 750 m.m. pressure. How much iron would ou require for the purpose? *Banaras* '22

Let 1000 litres of H_2 at 30°C and 750 m.m. occupy v litres at N.T.P.

$$\therefore\ \frac{1000\times750}{30+273}=\frac{v\times760}{273}\ \text{whence } v=889{\cdot}4 \text{ litres.}$$

(i) $\underset{3\times56}{3Fe}+4H_2O=Fe_3O_4+\underset{4\times22\cdot4}{4H_2}$ litres at N.T.P.

i.e., $4\times22{\cdot}4$ litre of H_2 at N.T.P. require 3×56 gm. of Fe

$\therefore$ 889·4 „ „ „ $(3\times56\times889{\cdot}4)/4\times22{\cdot}4$ or 1667 gm of Fe.

(ii) $\underset{56}{Fe}+H_2SO_4=FeSO_4+\underset{22\cdot4}{H_2}$ litres at N.T.P.

i.e., 22·4 litres of H_2 at N.T.P. require 56 gm. of Fe.

$\therefore$ 889·4 litres „ „ $(56\times889{\cdot}4)/22{\cdot}4$ or 2224 gm. of Fe.

$\therefore$ iron required is 1667 gm. or 2224 gm. according as Fe reacts with steam or acid.

9. Calculate the amount of $KClO_3$ which on complete decomposition will yield just sufficient oxygen for the complete combustion of 1520 c.c. of a gas mixture, consisting of 20 per cent methane and 80 per cent carbon monoxide at 27°C and 750 m.m. pressure. *Calcutta* '44.

Suppose the volume of the gas mixture is v c.c. at N.T.P.

$\therefore \ \dfrac{v \times 760}{273} = \dfrac{1520 \times 750}{300}$ whence $v = 1365$ c.c.

Vol. of $CH_4 = 1365 \times 0{\cdot}2 = 273$ c.c.; vol. of $CO = 1365 \times 0{\cdot}8 = 1092$ c.c.

(i) $CH_4 + 2O_2 = CO_2 + 2H_2O$
1 vol. 2 vols.

i.e., 1 c.c. of methane at N.T.P. is burnt by 2 c.c. of O_2 at N.T.P.

$\therefore$ 273 ,, ,, ,, are burnt by 546 c.c. of O_2 at N.T.P.

(ii) $2CO + O_2 = 2CO_2$
2 vol. 1 vol.

i.e., 2 c.c. of CO at N.T.P. are burnt by 1 c.c. of O_2 at N.T.P.

$\therefore$ 1092 c.c. ,, ,, ,, ,, ,, 546 c.c. of O_2 at N.T.P.

$\therefore$ total volume of oxygen required = 546+546 = 1092 c.c.

Now, $2KClO_3 = 2KCl + 3O_2$
245 gm. $3 \times 22{\cdot}4$ litres at N.T.P.

i.e., 3×22400 c.c. of O_2 are obtained from 245 gm. of $KClO_3$.

$\therefore$ 1092 c.c. ,, ,, ,, ,, $\dfrac{245 \times 1092}{3 \times 22400}$ or $3{\cdot}98$ gm.

10. Assuming air contains 23 per cent by weight of oxygen find out the volume of air, at 27°C and 750 m.m. pressure that would be required for complete combustion of one kilogram of coal, containing 90% C and 5% H.

1 kilogram = 1000 gms.

1 kilogram of coal contains 900 gms. of carbon and 50 gms. of hydrogen.

(i) $C + O_2 = CO_2$

i.e., 12 gms. of carbon require 32 gms. of O_2

$\therefore$ 900 gms. ,, ,, $(32 \times 900)/12$ *i.e.*, 2400 gms. of O_2

(ii) $2H_2 + O_2 = 2H_2O$

i.e., 4 gms. of hydrogen require 32 gms., of O_2

$\therefore$ 50 gms. ,, ,, $(32 \times 50)/4$ *i.e.*, 400 gms. of O_2

Hence total amount of oxygen required = (2400+400) *i.e.*, 2800 gms.

$\therefore$ 2800 gms of O_2 are present in $(2800 \times 100)/23$ gms. of air *i.e.*, 12170 gm., since air contains 23% O_2 by weight.

Now, the density of air (relative to H) = 14·4.

$\therefore$ weight of 1 litre of air at N.T.P. = $14{\cdot}4 \times 0{\cdot}09$ *i.e.*, 1·296 gm.

i.e., 1·296 gms. of air occupy 1 litre at N.T.P.

$\therefore$ 12170 gms. ,, ,, ,, 12170/1·296 *i.e.*, 9396 litres at N.T.P.

Let it occupy v litres at 27°C and 750 m.m. pressure.

$\dfrac{x \times 750}{27 + 273} = \dfrac{9396 \times 760}{273}$ whence $v = 10460$ litres.

11. H_2S obtained by treating a sample of ferrous sulphide with dilute sulphuric acid contained 5% of hydrogen by volume. What percentage of free iron did FeS contain?

Let the % of free iron in FeS be x

$\therefore$ 100 gms. of the sample contain (100−x) g. of FeS and x gm. of free Fe.

$FeS + H_2SO_4 = FeSO_4 + H_2S$
88 22·4 litres of H_2S at N.T.P.

$\therefore$ (100−x) gm. of FeS produce $22{\cdot}4 \times (100 - x)/88$ litres of H_2S at N.T.P.

$Fe + H_2SO_4 = FeSO_4 + H_2$
56 22·4 litres at N.T.P.

$\therefore$ x gm. of iron produce $22{\cdot}4x/56$ litres of H_2 at N.T.P.

But the ratio of H_2S to H_2 in the gas mixture is as 95 is to 5.

$$\frac{22{\cdot}4(100-x)}{88} : \frac{22{\cdot}4x}{56} = 95 : 5 \text{ whence } x = 3{\cdot}24 \quad \therefore \ \% \text{ of free Fe} = 3{\cdot}24.$$

12. Hydrogen obtained by the action of sulphuric acid on 10 gms. of zinc, is passed oved 50 gms. of pure and dry copper oxide. Find the weight of the residue and the volume of gaseous product at 100°C and 76 cm. pressure.
Calcutta '19.

(i) $Zn+H_2SO_4 = ZnSO_4+H_2$
65 — 2 gms. or 22·4 litres of H_2 at N.T.P.

∴ 10 gms. of Zn produce (22·4×10)/65 *i.e.*, 3·45 litres of H_2 at N.T.P. or (2×10)/65 or 0·3 gm. of H_2

(ii) $CuO+H_2 = Cu+H_2O$ (steam).

22·4 litres of H_2 at N.T.P. produce 22·4 litres of steam at N.T.P.

∴ 3·45 litres of H_2 at N.T.P. produce 3·45 litres of steam at N.T.P.

Let it occupy v litre at 100°C and 76 c.m. pressure :

$$\frac{v\times76}{273+100} = \frac{3{\cdot}45\times76}{273} \text{ whence } v = 4{\cdot}71 \text{ litres.}$$

(iii) $2H_2+O_2 = H_2O$
4 — 32

∴ 0·3 gm. of H_2 combines with (32×0·3)/4 *i.e.*, 2·4 gms. of O_2 which is taken from the copper oxide. Hence the weight of the residue =50−2·4=47·6 gms.

13. 1.3158 gms. of a sample of limestone was dissolved by heating in HCl in an air-free apparatus. The gas liberated was freed from acid vapour and dried, when its volume measured at 27°C and 750 m.m. was found to be 311·8 c.c. 1·0526 gms. of the *same* sample, when strongly heated till no more gas was given off, left a reside of 0·6126 gm. Calculate the density (mass per unit volume) of the gas at N.T.P. and its molecular weight. *Calcutta* '40.

Let 311·8 c.c. of the gas occupy v c.c. at N.T.P.

$$\frac{311{\cdot}8\times750}{273+27} = \frac{760\times v}{273} \quad \therefore \ v = 280 \text{ c.c.}$$

Now 1·3158 gms. of limestone liberate 280 c.c. of the gas at N.T.P.

∴ 1·0526 gms. of limestone liberate (280×1·0526)/1·3158 *i.e.*, 224 c.c. of the gas at N.T.P.

1·0526 gm. of limestone, after liberating 224 c.c. of the gas leave a residue of 0·6126 gm.

∴ 224 c.c. of the gas at N.T.P. weigh (1·0526−0·6126) i.e., 0·44 gm.

Hence density of the gas = 0·44/224 i.e., 0·001964 gm. per c.c. at N.T.P.

∴ 1 litre of the gas at N.T.P weighs 1·964 gms. or 22·4 litres (gram-molecular volume) weighs 1·964×22·4 i.e., 44 gms.

Hence the molecular weight of the gas is 44 gms.

14. A sample of 25 gms. of pure chalk were uniformly mixed with pure silica; 0·75 gms. of the mixture when treated with hydrochloric acid liberated 125 c.c. of CO_2, measured at 27°C and 756 m.m. pressure. Find the amount of silica that was mixed with the sample of chalk.

Suppose the volume of CO_2 at N.T.P. is v. c.c., then

$$\frac{v\times760}{273} = \frac{125\times756}{300} \text{ whence } v = 113{\cdot}2 \text{ c.c.}$$

$CaCO_3+2HCl = CaCl_2+H_2O+CO_2$
100 — 22400 c.c.

i.e., 22400 c.c. of CO_2 are liberated from 100 gms. of chalk.

∴ 113·2 c.c. „ „ 113·2/22·4 or 0·5 gm. of chalk.

∴ 0·75 gm. of the mixture contained 0·5 gm. of chalk, and hence 0·75 − 0·5 = 0·25 gm. of silica.

Hence, 0·5 gm. of chalk was mixed with 0·25 gm. of silica
or 25 gm. „ „ 12·5 gms.

∴ the amount of silica = 12·5 gms.

15. 5 c.c. of a solution of H_2O_2 liberated 0·508 gm. of iodine from KI solution. Calculate the strength of the hydrogen peroxide solution in terms of (a) grams per litre, and (b) 'volume' strength.

(a) $\underset{34}{H_2O_2} + 2HCl + 2KI = 2KCl + 2H_2O + \underset{254}{I_2}$

∴ 0·508 gm. of I_2 was liberated by (34×0·508)/254 or 0·068 g. of H_2O_2.

Hence the strength of the solution = (0·068×1000)/5 = 13·6 grams of hydrogen peroxide per litre. ∴ the solution is 1·36% strong.

(b) 1% solution is of "3·3 volume" strength

∴ 1·36% solution is of "1·36×3·3 volume" strength.

i.e., the strength is "4·48 volumes".

16. 0·0321 gm. of an impure sample of aluminium gave on treatment with dilute hydrochloric acid 39·3 c.c. of moist hydrogen measured at 13°C and 761 m.m. pressure. The impurity in the sample was alumina. Calculate the percentage of purity of the metal. Aqueous tension at 23°C = 11 m.m. *Cal.* '46.

Let the volume of hydrogen at N.T.P. be v c.c., then

$$\frac{2\times760}{273}=\frac{39·3\times(761-11)}{(273+13)},\ \text{whence } v = 37 \text{ c.c.}$$

$$\underset{2\times27\text{ gm.}}{2Al}+6HCl = 2AlCl_3+\underset{3\times22·4\text{ litres at N.T.P.}}{3H_2}$$

∴ 37 c.c. of hydrogen correspond to (2×27×37)/3×22400 gms. of aluminium, i.e., 0·02973 gm. of Al.

Hence, the impurity = (0·0321 − 0·02973) = 0·00237

∴ the % of impurity = (0·00237×100)/0·0321 = 7·38%.

17. Calculate the percentage of potassium chlorate in a commercial sample of the material, contaminated with potassium chloride, 1·555 gms. of which liberate, when fully decomposed, just sufficient oxygen for the complete combustion of 152 c.c. of acetylene gas at 27°C and 750 m.m. pressure. *Calcutta* 1949.

Let the volume of acetylene at N.T.P. be v c.c., then

$$\frac{v\times760}{273}=\frac{152\times750}{300},\ \text{whence } v = 136·6 \text{ c.c.}$$

From the equation: $2C_2H_2+5O_2 = 4CO_2+2H_2O$. 2 c.c. of acetylene are burnt by 5 c.c. of oxygen. Hence the volume of oxygen required:

= (5×136·6)/2 = 341·5 c.c.

Now, $\underset{245}{2KClO_3} = 2KCl+\underset{3\times22400\text{ c.c.}}{3O_2}$

i.e., 3×22400 c.c. O_2 are obtained from 245 gms. of $KClO_3$

∴ 341·5 c.c. of O_2 „ „ (245×341·5)/3×22400 or 1·246 gm. of $KClO_3$.

∴ % of $KClO_3$ in the sample = (1·246×100)/1·555 = 80·13%.

---

18. How many c.c.'s of hydrogen and oxygen at 10°C and 770 mm. pressure can be obtained from 1 gram of water? H 1273 c.c.; O 636·5 c.c.

19. What weight of potassium chlorate is required to yield oxygen sufficient to burn the hydrogen evolved by the action of water upon 230 gms. of sodium? 204·2 gm.

20. How much marble and hydrochloric acid containing 22 per cent HCl are required to give 10 litres of CO_2 at 15°C and 760 m.m. pressure? 42·32 gm. marble; 140·5 gm. HCl solution.

21. 2·5 litres of nitrous oxide are collected at 39°C and 741 mm. pressure. What weight of ammonium nitrate are decomposed in order to supply the gas? 7·6 gm.

22. 5 gms. of manganese dioxide are heated with excess of HCl. The chlorine evolved is passed into potassium iodide solution. Calculate the weight of iodine liberated. *Bombay* '14. 14·60 gms.

23. 0·2925 gm. of a specimen of common salt from Khewrah mines was dissolved in water and competely precipitated by a solution of silver nitrate. The precipitate after washing and drying was found to weigh 0·7075 gm. What was the percentage of sodium chloride in the specimen? Ag = 108, Cl = 35·5. *Bombay* '10. 98·63 p.c.

24. What weight of sulphuric acid would be required to convert the sodium chloride, obtained from 2 litres of sea water, completely into sodium sulphate? Sea-water contains 3·42 per cent by weight of common salt. Density of sea-water = 1·04. *Allahabad* '20. 59·58 gms.

25. 5 gms. of potassium chloride were heated with enough conc. H_2SO_4 and manganese dioxide. The evolved gas was led into 5 gms. of caustic soda in 50 c.c. of water. When the experiment is over what will be the composition of the alkali solution? NaCl, 1·963; NaOCl, 2·5; NaOH, 2·315 gms. *Calcutta* '40.

26. The temporary hardness of a sample of water can be removed by adding 10 milligrams of lime per litre; find the number of milligrams of calcium salt in the sample. *Nagpur* '26. 28·93 mg. per litre.

27. 6 gms. of a mixture of potassium chlorate and chloride on ignition left 4·0450 gm. of the chloride. Find out the percentage of chloride in the original mixture. 16·88

28. 20 c.c. of a solution of KCl containing some NaCl gave on evaporation 1·873 gms. of the mixed salts which gave 3·731 gms. of silver chloride by reaction with silver nitrate. Calculate the quantity of NaCl in 10 c.c. of the solution. (K = 39·1; Ag = 108; Cl = 35·5; Na = 23). 0·1218 gm. NaCl.

29. Three grams of a mixture of anhydrous sodium carbonate and sodium bicarbonate lost 0·348 gm. on heating. Calculate the percentage of sodium carbonate in the mixture. 68·567.

30. Calculate the quantity of pyrolusite, containing 60% by weight of manganese dioxide, which would be required to liberate sufficient chlorine from HCl to make 10 gms. of anhydrous ferric chloride from the metal. Assume that 10% of the available chlorine is wasted. 14·9 gms.

31. 30 gms. of $KClO_3$ are heated to produce oxygen. What weight of zinc will be required to generate sufficient hydrogen to completely combine with the oxygen liberated? Zn = 65·4. 48·0 gms.

32. Calculate the volume of hydrogen at 27°C and 750 mm pressure that would be produced in each of the following cases by the decomposition of 5·4 gms. of water when (a) water is acted upon by sodium, (b) water reacts with calcium hydride, (c) steam is passed over red hot iron. (a) 3·74; (b) 7·48; (c) 7·48 litres. *Calcutta* '41.

33. How much sulphuric acid would be needed to neutralise the ammonia produced from 107 gm. of chemically pure ammonium chloride? What would be the volume of ammonia, if liberated and collected at 37°C when the barometric pressure was 760 mm. and the vapour tension of liquid over which ammonia was collected was 2·3 mm.? 98 gms., 51.04 litres. *Calcutta* '37.

34. 1 gm. of a mixture of sodium carbonate and sodium bicarbonate, in equal proportions by weight, is ignited until there is no more loss in weight. What volume of CO_2 is evolved at N.T.P.? 66·6 c.c. *Nagpur* '34.

35. Air contains 23 per cent oxygen by weight. Its density (H=1) is 14·4. What volume of air at N.T.P. is required to convert 1 gram of carbon into producer gas (CO and N_2)? 4·474 *l.*

36. A balloon of 1000 litres capacity is to be filled with hydrogen at 27°C and 750 mm. pressure. Calculate the minimum quantity of iron required to liberate the necessary amount of hydrogen. *Calcutta '25.*
1684 gms. of Fe by steam-iron process.

37. What weights of zinc and sulphuric acid are required to produce enough hydrogen to reduce completely 8·5 gms. of cupric oxide to copper?
(Cu=63·5, Zn=65·4). Zn 6·99 gm.; acid 10·47 gm. *Punjab* 1944.

38. A sample of dolomite contained 54% $CaCO_3$ and 42% $MgCO_3$ and 4% clay. Calculate volume of CO_2 measured at 10°C and 750 mm. which would be evolved on heating 5 gm. of the sample with HCl.
1·224 litres. *Punjab* 1934.

39. Ferrous sulphide containing some free iron is decomposed by HCl to give a mixture of H_2 and H_2S. The gas mixture on treatment with alkali decrease in volume to one-tenth. Calculate the percentage by weight of free iron in ferrous sulphide. 6·60 per cent.

40. Calculate the volume of a solution of sulphuric acid of density 1·8 and containing 89% of pure acid that would be required to make 2000 c.c. of SO_2, measured at N.T.P., by acting on sodium sulphite.

Andhra University. 5·46 c.c.

41. A certain coal contains 2·20 per cent of sulphur by weight. What volume of sulphur dioxide at N.T.P. is evolved when 1 ton of this coal is burnt?
15640 litres.

42. Calculate the quantity of pure $CaCO_3$ from which one litre of CO_2 at 27°C and normal pressure may be prepared. What weight of pure carbon would yield the same quantity of CO_2? *Calcutta* '29.

$CaCO_3$, 4 gm.; Carbon 0·49 gm.

43. Calculate the weight of copper and the volume of nitric acid required for the preparation of 5 litres of nitric oxide, measured at 20°C and 755 mm. pressure assuming that no side reactions take place. The nitric acid supplied has a density of 1·42 and contains 61 per cent by weight of real nitric acid.

Inter Board, U. P. 19·7 gms. Cu; 60·12 c.c. HNO_3

44. 25 c.c. of potassium permanganate solution containing 6 gms. per litre, were required to react with 20 c.c. of a solution of H_2O_2 in the presence of dilute H_2SO_4. Calculate the volume of oxygen measured at 20°C and 750 mm. pressure which would be liberated from 100 c.c. of the H_2O_2 solution by the action of finely divided platinum. 144·5 c.c.

45. 3·00 gm. of a mixture of zinc powder and zinc oxide were attacked by an excess of dilute H_2SO_4 to give 600 c.c. of hydrogen, measured over water at 17°C and 750 mm. What p.c. of pure zinc atoms in the mixture were combined with oxygen? Zn=65·4; aqueous vapour=14 mm. at 17°C. 41·4%.

46. 1 gm. of zinc containing ZnO as impurity, gave on treatment with dilute acid 130 c.c. dry H_2 at 50°C and 755 mm. pressure. Calculate percentage of zinc in the impure specimen. Zn=65·3. *London Matric.* 31·82%.

47. What products would be obtained, and what weight of each, when 10 grams of (a) potassium chlorate, and of (b) white marble are separately heated to redness until no further change occurs?

6·1 gms. of KCl; 3·9 gms. of O_2; 5·6 gms. of CaO; 4·4 gms. of CO_2.

48. A solution was known to contain both nitric and hydrochloric acids. For complete neutralisation it was found that 50 c.c. of the acid solution required 42 c.c. of caustic soda solution containing 25 gms. per litre, whilst on precipitation with silver nitrate 50 c.c. yielded 2·45 gms. of silver chloride. Calculate the weights of hydrochloric and nitric acid, respectively, contained in 1 litre of the solution. (Ag=108). 12·46 gms. HCl; 11·57 gms. HNO_3.
London Matric.

49. Find the weight of $KClO_3$ necessary to prepare 1 litre of oxygen at 27°C and 750 mm. pressure. 3·275 gms. $KClO_3$.

50. What volume of carbon dioxide could be obtained by dissolving 3 gms. pure marble in hydrochloric acid? What volume would the gas occupy at 16°C and 750 mm.? 672 c.c., 720·7 c.c.

51. In order to determine the strength of a sample of HCl of sp. gr. 1·55, 10 c.c. were taken and added to 7·5 gms. of marble; after all the action has ceased. 2·664 gm. of marble was left undissolved Calculate the percentage by weight of hydrochloric acid in the sample of the aaid *London matric.* 22·78 p.c.

52. A diad metal forms several oxides; it was found that when 411 gms. of an oxide (containing 9·34 per cent of oxygen) were heated with nitric acid 397·2 gms. of the nitrate had been formed, whilst 143·4 gms. of another oxide (containing 13·39 per cent of oxygen) were left undissolved. Calculate the formulæ of the oxides and the atomic weight of the metal, and write out the equation represeting the reaction which took place.

M_3O_4; MO_2; atomic weight 207.

53. 1·000 gm. of a mixture of the carbonates of calcium and magnesium gave 240 c.c. of CO_2 at N.T.P. Calculate the composition of the mixture.

62·5% $CaCO_3$; 37·5% $MgCO_3$.

54. 4·5 gms of water are (a) decomposed by sodium; (b) passed as steam over read hot iron; (c) decomposed by an electric current. What volume of gas at N.T.P. is produced in each case? 2·8 litres; 5·6 litres; 8·4 litres. *Calcutta* '27.

55. How much ammonia would you get from 1 gm. of NH_4Cl at 15°C and 740 m m.? *Calcutta* '16. 453·5 c.c.

56. What volume of H_2S at 20°C and 720 mm. is required to convert 1 gm. of copper sulphate, $CuSO_4.5H_2O$, into copper sulphide? How much ferrous sulphide would be required to yield the requisite volume H_2S?

0·1017 *l.* of H_2S; 0·353 gm. of FeS.

57. When steam is passed over heated carbon a mixture of hydrogen and carbon monoxide is formed. What volume of the gas would be obtained from 1 kilogram of carbon? 3733 litres.

58. An impure specimen of magnesium carbonate was found to lose 16% by weight on heating. What was the percentage purity of the sample if the only other substance was sand? 30·5% $MgCO_3$.

59. A solution of sodium carbonate containing 21·2 gms. of the anhydrous salt and 100 gms. of water is treated with a slow current of CO_2 until no further action takes place. Write an equation for the reaction that takes place, and calculate what amount of sodium bicarbonate will be thrown out of the solution during the passage of the gas, the solubility of the bicarbonate being 9 gms. in 100 gms. of water at the temperature of the experiment. 24·6 gms. deposited.

60. When 1·225 gms. of potassium chlorate was strongly heated, 336 c.c. of oxygen were evolved at N.T.P., and the residue weighed 0·745 gm. What is the density of oxygen, and its molecular weight? 1·43 gms. per litre; 32.

61. 25 c.c. of '20 volume' hydrogen peroxide are added to a solution of potassium iodide. What weight of iodine is liberated? 11·32 gms.

62. What volume of oxygen at 12°C and 780 mm. will be required to burn all the hydrogen evolved by the action of dilute HCl on 25 gms. of zinc?

Zn = 65·5 *Calcutta* '08. 4·35 litres.

63. A quantity of carbon monoxide is passed through red-hot tube containing ferric oxide. The resulting gas is absorbed in caustic potash. The gain in weight of caustic potash was 0·86 gm. What was the volume of CO at N.T.P.?

437·8 c.c.

64. What volume of air at 27°C and 750 mm. would be required for the complete combustion of 100 volumes of a gaseous mixture containing 46% H_2, 40% CH_4, 14% CO by volume? Air contains 79% N_2 and 21% O_2 by volume.

Calcutta '21. 523·3 vols.

65. How much H_2SO_4 is required to decompose 100 gms. of chalk and how much $CaSO_4$ is produced? What is the volume of the gas produced at N.T.P.?
98 gms. H_2SO_4; 136 gms. $CaSO_4$; 22·4 *l.* CO_2.

66. How many tons of H_2SO_4 can theoretically be obtained from 500 tons pyrites containing 48% of sulphur? 735 tons.

67. How much pyrolusite (82% MnO_2), and how much hydrochloric acid (33% HCl) will be required to furnish the chlorine necessary to convert 40 gms. of potassium hydroxide completely into chlorate and chloride?
38 grams; 158 grams.

68. A mixture of KCl and KI is converted into potassium sulphate, and the weight of the sulphate is found to be the same as that of the original mixture. In what proportions were the salts present in the mixture?
74% KCl; 26% KI.

68. Give equations representing the formation of hydrogen by the action of (a) steam, (b) dilute H_2SO_4 on iron. What weight of iron would be necessary in each case for the preparation of 300 litres of hydrogen measured at 27°C and 740 mm. pressure? 498·6 gm.; 664·8 gm.

69. Calculate the volume of nitrous oxide, measured at N.T.P., obtainable from 20 gms. of ammonium nitrate, and the volume of nitrogen it would contain.
5·6 litres in each case.

70. What weight of common salt would be required to furnish sufficient hydrogen chloride to neutralise 100 gms. of a 30% solution of caustic soda? What would be the volume of the gas at N.T.P.? 43·9 gms.; 16·8 litres.

71. It was found that 224 c.c. of SO_2 at N.T.P. just decolourised 100 c.c. of a solution of $KMnO_4$ in dilute sulphuric acid. Calculate the strength of the potassium permanganate solution in grams per litre. 6·32 gms. per litre.

72. In order to determine the strength of dilute sulphuric acid having the density 1·091, 2 gms. of pure magnesite were treated with 10 c.c. of the acid. After all action had ceased it was found that 0·8743 gm. of magnesite remained undissolved. Calculate the number of gms. of H_2SO_4 in (a) a litre, (b) a kilogram, of the dilute acid. What volume of CO_2 at 13°C and 740 mm. pressure would be produced in the above reaction? 131·3 gms.; 120·3 gms; 322·8 c.c.

73. Calculate the volume of air at 30°C and 750 mm. pressure that will be required for the complete combustion of 5 gms. of a sample of pyrites containing 40 per cent of sulphur assuming that air contains 20 per cent of oxygen by volume. *Calcutta* 1950. 7·8 litres.

Eudiometry

Eudiometry refers to reactions taking place in the gas phase only and hence is concerned with the *analysis of gases* and *volumetric composition of gaseous compounds.* The equation:

$$2H_2 + O_2 = 2H_2O \text{ (steam)}$$

signifies that 2 gram molecules of hydrogen combine with 1 gram molecule of oxygen to form 2 gram molecules of steam, or 2 × 22·4 litres of hydrogen combine with 22·4 litres of oxygen to form 2 × 22·4 litres of steam—*the volumes being all measured at N.T.P.*

∴ the *relative* volumes of hydrogen, oxygen and steam in the above reaction is H_2: O_2: steam is *2 : 1 : 2 by volume.*

In eudiometry, for comparison of volumes of gases involved in a reaction, the knowledge of their relative volumes (and not of the actual volumes) is required, and *for convenience 1 gram-molecule of a gas is supposed to occupy one volume* (which, however, stands for 22·4 litres at N.T.P.). Hence the equation $2H_2 + O_2 = 2H_2O$ (steam) shows that 2 volumes of hydrogen unite with one volume of oxygen to give 2 volumes of steam.

Illustrations.—(i) $2H_2 + O_2 = 2H_2O$ (steam) Contraction
2 vols. 1 vol. 2 vols. 1 volume

When the temperature of the eudiometer is below 100°C, steam condenses into water of negligible volume, and hence *the contraction becomes 3 volumes.*

2/3rds the contraction = the volume of hydrogen;

1/3rd the contraction = the volume of oxygen.

(ii) $CH_4 + 2O_2 = CO_2 + 2H_2O$ (liquid) Contraction
1 vol. 2 vols. 1 vol. 0 vol. 2 volumes.

(iii) $2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$ (liquid)
2 vols. 5 vols. 4 vols. 0 vol. 3 volumes.

(iv) $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$ (liquid)
1 vol. 3 vols. 2 vols. 0 vol. 2 volumes.

(v) $CO_2 + C$ (solid) $= 2CO$ Expansion.
1 vol. 0 vol. 2 vols. 1 volume

(vi) $N_2 + O_2 = 2NO$ No change in volume.
1 vol. 1 vol. 2 vols.

The volume occupied by a *liquid* or a *solid* is negligibly small compared with that of a gas; they are, therefore, supposed to occupy *zero volume* in eudiometry.

In *gas analysis* the volumes of gases, may be found out by absorption with suitable absorbents.—(i) *caustic potash for CO_2 and other acid gases*, (ii) *alkaline pyrogallate for oxygen*, (iii) *ammoniacal cuprous chloride for CO and acetylene*, and (iv) *fuming H_2SO_4 or bromine water for ethylene.* Volume of methane is found out by explosion with oxygen.

The formula of gaseous hydrocarbons.—The formula of a gaseous hydrocarbon is determined by exploding a known volume of it with excess oxygen—the immediate contraction on explosion and also the contraction that occurs when caustic potash is admitted (thus absorbing the carbon dioxide formed) are being noted.

Contraction on explosion = (volume of gases before explosion)
− (volume of gases after explosion)

i.e., contraction = (vol. of hydrocarbon + vol. of oxygen *taken*)—(vol. of carbon dioxide formed + vol. of oxygen *left unused*).

or contraction = vol. of hydrocarbon + (vol. of oxygen *taken*—vol. of oxygen *left* unused)—vol. of carbon dioxide formed.

∴ Contraction = (Vol. of HC + Vol of O_2 used) — Vol of CO_2 formed

∴ **contraction on explosion = vol. of hydrocarbon + vol. of oxygen actually used up − vol. of carbon dioxide formed.**

or Suppose the hydrocarbon is CxHy when *x* and *y* stand for atoms of carbon and hydrogen respectively.

Let the volume of hydrocarbon exploded = *m* c.c.
the contraction on explosion = *p* c.c.
the volume of CO_2 formed = *n* c.c.

The equation for the reaction which occurs on explosion is :

$$CxHy + (x+y/4)\ O_2 = x\ CO_2 + y/2\ H_2O.$$

1 volume of CxHy uses up $(x+y/4)$ volumes of oxygen and produces *x* volumes of CO_2 after combustion—there being an accompanying contraction during explosion.

i.e., 1 vol. of CxHy+(x+y/4) vol. *of* $O_2=x$ vol., of CO_2+ contraction.

∴ *m* vol. of CxHy+*m*(x+y/4) vol. of $O_2=mx$ vol. of CO_2+ contraction (*p* cc.). ∴ $m+m(x+y/4)=mx+p$

or $m\ (1+y/4)=p$; ∴ $y=4\ (p/m-1)$; also $n=mx$ ∴$x=n/m$.

Substituting the values of *m*, *p* and *n* from actual experimental data, the formula is deduced.

Exercises

1. 20 c.c. of a gaseous hydrocarbon were exploded with excess of O_2. The contraction observed was 30 c.c. There is a further contraction of 40 c.c. on treatment with KOH. What is the molecular formula of the hydrocarbon? *Calcutta* '48.

Contraction = vol. of the hydrocarbon + vol. of O_2 used up—vol. of CO_2 formed.

∴ 30 = 20 + vol. of O_2 used up −40. ∴ vol. of O_2 used up = 50 c.c.

Now. CO_2 contains its own volume of O_2. $C + O_2 = CO_2$.

∴ 40 c.c. CO_2 formed contain 40 c.c. O_2, i.e., 40 c.c. of O_2 were used to oxidise the carbon in the hydrocarbon.

∴ the oxygen used in oxidising the hydrogen of the hydrocarbon = (50−40) = 10 c.c.

∴ vol. of hydrogen = twice the volume of $O_2 = 2\times10 = 20$ c.c.

20 c.c. of the hydrocarbon contain this 20 c.c. of hydrogen.

Hence, 20 c.c. of the hydrocarbon contain 20 c.c. of H_2 and give 40 c.c. of CO_2.

∴ 1 c.c. of the hydrocarbon contains 1 c.c. of H_2 and gives 2 c.c. of CO_2.

or, 1 molecule of the hydrocarbon contains 1 molecule of hydrogen and give 2 molecules of CO_2.

Now, 1 molecule of hydrogen consists of 2 atoms of hydrogen and 1 molecule of CO_2 contains 1 atom of carbon. ∴ the formula is C_2H_2.

or, suppose the hydrocarbon is CxHy, then $x=n/m$; $y=4(p/m-1)$.

m = vol. of CxHy = 20 c.c.; p = contraction = 30 c.c.; and

n = volume of CO_2 = 40 c.c.

∴ $x = 40/20 = 2$; $y = 4(30/20-1) = 2$. Hence the formula is C_2H_2.

2. Nitric oxide alone does not explode with hydrogen, but does so when mixed with an equal volume of nitrous oxide. 20 c.c. of each of these oxides mixed with 40 c.c. of hydrogen were exploded. All the hydrogen was used up and 30 c.c. of nitrogen produced. Find the formula of nitric oxide, if that of nitrous oxide be N_2O.

Nitrous oxide reacts with hydrogen as $\underset{1\text{ c.c.}}{N_2O} + \underset{1\text{ c.c.}}{H_2} = H_2O + \underset{1\text{ c.c.}}{N_2}$

∴ 20 c.c. of N_2O consume 20 c.c. of H_2 and produce 20 c.c. of N_2.

∴ the nitrogen produced from nitric oxide = (30−20) = 10 c.c.

20 c.c. of H_2 were used by nitrous oxide, and hence vol. of H_2 used by nitric oxide = (40−20) = 20 c.c. But 20 c.c. of H_2 can react with 10 c.c. of O_2 only.

Hence 20 c.c. of nitric oxide contain 10 c.c. of O_2 and 10 c.c. of N_2.

Or, 1 c.c. of nitric contains $\frac{1}{2}$ molecule of O_2 and $\frac{1}{2}$ c.c. of N_2.

∴ 1 molecule of nitric oxide contains $\frac{1}{2}$ molecule of O_2 and $\frac{1}{2}$ molecule of N_2. ∴ the formula is NO.

3. 25 c.c. of oxygen are subjected to silent electric discharge and the volume of ozonised oxygen becomes 20 c.c. What is the composition of the ozonised oxygen?

Let the vol. of O_3 be x c.c. $\therefore$ vol. of O_2 in the mixture = $(20-x)$ c.c. Ozonisation of oxygen takes place as : $\underset{3 \text{ c.c.}}{3O_2} \rightleftharpoons \underset{2 \text{ c.c.}}{2O_3}$

$\therefore$ x c.c. of ozone yield $3x/2$ c.c. of oxygen.

$\therefore$ $3x/2+(20-x) = 25$, whence $x = 10$,

$\therefore$ vol. of O_2 = 10 c.c.; vol. of O_3 = 10 c.c.

4. 25 c.c. of marsh gas at N.T.P. are mixed with 300 c.c. of air at 27°C and 750 mm. pressure and the mixture is exploded by electric sparks. Find out the volume of the residual gas at [illegible]°C and 750 mm. pressure. Air contains 20% O_2 and 80% N_2 by volume. 17 *Calcutta* '16.

Let 300 c.c. of air at 27°C and 750 mm. occupy v c.c. at N.T.P.

$\therefore$ $\frac{v \times 760}{273} = \frac{30 \times 750}{300}$ whence v = 269·4 c.c.,

269·4 c.c. of air contains $\frac{20 \times 269{\cdot}4}{100}$ or 53·88 c.c. of O_2 and $\frac{80 \times 269{\cdot}4}{100}$ or 215·52 c.c. of nitrogen at N.T.P.

The reaction involved is $\underset{1 \text{ c.c.}}{CH_4}+\underset{2 \text{ c.c.}}{2O_2} = 2H_2O+\underset{1 \text{ c.c.}}{CO_2}$

$\therefore$ 25 c.c. CH_4 consumes 50 c.c. of O_2 and yield 25 c.c. of CO_2.

$\therefore$ the volume of the oxygen left unused = (53·88−50) = 3·88 c.c. Final volume of the gas mixture = 215·52 c.c. of N_2 + 3·88 c.c. of O_2 + 25 c.c. of CO_2 = 244·4 c.c., at N.T.P.

Let the mixture occupy v c.c. at 17°C and 750 mm.

$\therefore$ $\frac{v \times 750}{290} = \frac{244{\cdot}4 \times 760}{273}$ whence v = 265 c.c.

5. One litre of a mixture of CO and CO_2 is found to give 1600 c.c. of CO, on being passed through a tube containing red-hot charcoal, both measured under the same conditions. Calculate the composition of the mixture. *Calcutta* '14.

Let the vol. of CO_2 in the mixture be x c.c., $\therefore$ vol. of CO is $(1000-x)$ c.c.

The reduction of CO_2 takes place as follows :

$$\underset{1 \text{ c.c.}}{CO_2} + C = \underset{2 \text{ c.c.}}{2CO}$$

$\therefore$ x c.c. of CO_2 yield $2x$ c.c. of CO. $\therefore$ CO produced from CO_2+CO originally present = $2x + (1000-x) = 1600$, where $x = 600$ c.c.

$\therefore$ vol. of CO_2 = 600 c.c., and the vol. of CO = 400 c.c.

6. 10 c.c. of a mixture of CO, CH_4 and N_2 exploded with excess of oxygen, gave a contraction of 6·5 c.c.; there was a further contraction of 7 c.c. when the residual gas was treated with KOH. What was the composition of the gas mixture? *Allahabad* '11.

Let the vol. of CO be x c.c. and that of CH_4 y c.c. $\therefore$ the vol. of N_2 = $(10-x-y)$ c.c. The reactions are :

(i)	2CO	+	O_2	=	$2CO_2$		contraction		
	2 c.c.		1 c.c.		2 c.c.		1 c.c.		
or	x c.c.				x c.c.		$x/2$ c.c.		
(ii)	CH_4	+	$2O_2$	=	CO_2	+	$2H_2O$		contraction
	1 c.c.		2 c.c.		1 c.c.				2 c.c.
or	y c.c.				y c.c.				$2y$ c.c.

$\therefore$ the total contraction = $x/2+2y$ = 6·5, and total vol. of CO_2 formed = $x+y$ = 7. Solving the equations, x = 5 and y = 2.

vol. of CH_4 = 2 c.c.; vol. of CO = 5 c.c.; vol. of N_2 = 3 c.c.

7. 100 c.c. of a mixture of nitrous and nitric oxide are slowly passed over red-hot copper. The resulting gas occupied a volume of 85 c.c., both measured under the same conditions; 20 c.c. of oxygen were added to another 100 c.c. of the same mixture and the volume contracted in this case from 120 c.c. to 105 c.c. Assuming that the NO is converted into NO_2, find the composition of this 105 c.c. of gas mixture.

Let the volume of NO be x c.c., that of N_2O, therefore, = $(100-x)$ c.c.

The reactions are:

$$\begin{array}{llcll} \text{(i)} & 2NO + 2Cu & = & 2CuO & + \; N_2 \\ & 2 \text{ c.c.} & & & \;\; 1 \text{ c.c.} \\ & \text{or } x \text{ c.c.} & & & \;\; x/2 \text{ c.c.} \\ \text{(ii)} & N_2O + Cu & = & CuO & + \; N_2 \\ & 1 \text{ c.c.} & & & \;\; 1 \text{ c.c.} \\ & \text{or } (100-x) \text{ c.c.} & & & \;\; (100-x) \text{ c.c.} \end{array}$$

∴ total volume of nitrogen = $x/2+(100-x) = 85$, whence $x = 30$.

∴ the mixture contains 30% NO and 70% N_2O.

$$\begin{array}{lccccc} \text{The reaction in the second stage,} & 2NO & + & O_2 & = & 2NO_2 \\ & 2 \text{ c.c.} & & 1 \text{ c.c.} & & 2 \text{ c.c.} \\ & \text{or } 30 \text{ c.c.} & & 15 \text{ c.c.} & & 30 \text{ c.c.} \end{array}$$

i.e., 30 c.c. of NO react with 15 c.c. of O_2, producing 30 c.c. of NO_2.

∴ O_2 left unused = $(20-15) = 5$ c.c., ∴ the final 105 c.c. of the gas mixture = 70 c.c. N_2O+30 c.c. NO_2+5 c.c. O_2.

8. A gaseous mixture contains 50% H_2, 40% CH_4 and 10% O_2. Calculate the volume of additional oxygen at N.T.P. that will be required for the complete combustion of 200 c.c. of the above gas mixture measured at 27°C and 750 mm. pressure. *Calcutta* 1942.

Let the volume of the gas mixture be v c.c. at N.T.P.

Then, $\dfrac{v \times 760}{273} = \dfrac{200 \times 750}{273+27}$, ∴ $v = 179{\cdot}5$ c.c. at N.T.P.

∴ vols. of gases at N.T.P.: $H_2 = 179{\cdot}5 \times 50/100 = 89{\cdot}75$ c.c.;

$CH_4 = 179{\cdot}5 \times 40/100 = 71{\cdot}80$ c.c.; $O_2 = 179{\cdot}5 \times 10/100 = 17{\cdot}95$ c.c.

Now, $2H_2 + O_2 + 2H_2O$, i.e., 1 c.c. H_2 needs $\frac{1}{2}$ c.c. O_2 for combustion.

∴ $89{\cdot}75$ c.c. H_2 need $44{\cdot}875$ c.c. oxygen for combustion.

$CH_4+2O_2 = CO_2+2H_2O$, i.e., 1 c.c. CH_4 needs 2 c.c. O_2 for combustion.

∴ $71{\cdot}8$ c.c. CH_4 needs $143{\cdot}6$ c.c. oxygen for combustion.

∴ total oxygen required = $44{\cdot}875 + 143{\cdot}60 = 188{\cdot}475$ c.c. at N.T.P.

Additional oxygen required = $(188{\cdot}475-17{\cdot}95) = 170{\cdot}525$ c.c. at N.T.P.

9. To a mixture of acetylene, hydrogen, and carbon monoxide, occupying 20 c.c., 50 c.c. of oxygen were added and a spark passed. After cooling, the residual gases contained 16 c.c. of carbon dioxide and 36 c.c. of unburnt oxygen. What was the composition of the mixture?

Let the vol. of C_2H_2 be x c.c. and that of H_2 y c.c. ∴ the volume of $CO = 20-x-y$.

$$\begin{array}{llcccccc} \text{The reactions involved are:} & \text{(i)} & C_2H_2 & + & 5/2\,O_2 & = & 2CO_2 & + \; H_2O. \\ & & 1 \text{ c.c.} & & 5/2 \text{ c.c.} & & 2 \text{ c.c.} & \\ & & \text{or } x \text{ c.c.} & & 5x/2 \text{ c.c.} & & 2x \text{ c.c.} & \end{array}$$

$$\begin{array}{lllllllll} \text{(ii)} & H_2 + \frac{1}{2}O_2 = H_2O & & \text{(iii)} & CO & + & \frac{1}{2}O_2 & = & CO_2 \\ & 1 \text{ c.c.} \;\; \frac{1}{2} \text{ c.c.} & & & 1 \text{ c.c.} & & \frac{1}{2} \text{ c.c.} & & 1 \text{ c.c.} \\ & y \text{ c.c.} \;\; y/2 \text{ c.c.} & & \text{or} & (20-x-y) \text{ c.c.} & & \frac{1}{2}(20-x-y) \text{ c.c.} & & (20-x-y) \text{ c.c.} \end{array}$$

∴ carbon dioxide formed = $2x + (20-x-y) = 16$ or $y-x = 4$

Oxygen used up = $\dfrac{5x}{2} + \dfrac{y}{2} + \dfrac{20-x-y}{2} = 14$, or $4x = 8$, ∴ $x = 2$

and $y = 2$, ∴ composition is 2 c.c. C_2H_2; 6 c.c. H_2; 12 c.c. CO

10. A mixture of oxygen and carbon monoxide is exposed to the action of ultraviolet light. Ozone and carbon dioxide are the new gases formed in the reaction. If 100·000 c.c. of gas were taken in which the ratio O_2/CO was 1·015, how many c.c. of each will be found in the residue which measures 85·87 c.c. and has the ration $CO_2/CO = 0·2419$?

Let 100 c.c. of the gas mixture contain x c.c. of oxygen.

Then $\frac{O_2}{CO} = \frac{x}{100-x} = 1·015$, whence x = 50·36.

∴ vol. of O_2 = 50·36 c.c.; vol. of CO = 49·64 c.c.

Let m and n be vols. of O_2 and CO converted into O_2 and CO_2 respectively.

(i) $3O_2 \rightleftharpoons 2O_3$ contraction

3 vols. 2 vols. 1 volume

or m vol. 2*m*/3 vol. *m*/3 volumes

(ii) $CO + \frac{1}{2}O_2 = CO_2$ contraction

1 vol. $\frac{1}{2}$ vol. 1 vol. $\frac{1}{2}$ volume

or n vol. n/2 vol. n vol. *n*/2 volume

∴ total contraction = $m/3+n/2$ = 100 − 85·87 = 14·13; or $2m+3n$ = 84·78

Now, $\frac{\text{vol. of } CO_2 \text{ formed}}{\text{vol. of CO left}} = \frac{n}{49·54-n} = 0·2419$, ∴ n = 9·663.

Again, 2m+3n = 84·78, or 2m+3×9·663 = 84·78, whence m = 27·895.

The residue contains: O_2 = (50·36−m−n/2) = 17·634 c.c.'s; O_3 = 2m/3 = 18·596 c.c.

CO_2 = n = 9·663 c.c.; CO = 49·64−n = 39·977 c.c.; Total 85·87 c.c.

---

11. 12 c.c. of a gaseous hydrocarbon were mixed with 90 c.c. of O_2 and the mixture exploded in an eudiometer; after explosion the volume of mixture was 72 c.c. and on adding KOH 36 c.c. of it disappeared, leaving only O_2. What was the gas? *Patna* '29. C_3H_6.

12. 20 vols. of a hydrocarbon, mixed with 80 vols. of O_2, gave 60 vols. after explosion and 20 vols. after shaking with KOH solution. What was the gas? *Calcutta*. C_2H_4.

13. 20 c.c. of a hydrocarbon were exploded with 250 c.c. of air. The immediate contraction was 40 c.c. and the volume of CO_2 found by KOH absorption was 20 c.c. What is the composition of the hydrocarbon? *Calcutta* '32. CH_4.

14. Find the composition of ammonia from the following data—volume of ammonia taken = 22·5 c.c.; volume after sparking for sometime = 45 c.c.; volume after addition of oxygen = 188·5 c.c.; volume after explosion = 137·88 c.c.

15. Find the composition of nitrous oxide from the following data (the volumes are reduced to N.T.P.)—volume of gas taken = 10 c.c.; vol. after addition of H_2 = 28 c.c.; vol. after explosion = 18 c.c.; volume after addition of O_2 = 27 c.c.; volume after second explosion = 15 c.c. *Calcutta* '19.

16. 40 c.c. of a mixture of CO and C_2H_2 gases were mixed with 100 c.c. O_2 in an eudiometer and fired. After cooling the residual gas occupied 104 c.c.; and after treatment with KOH the residual gas occupied 48 c.c. Find the composition of the original mixture. *Allahabad* [illegible] CO 60%; C_2H_2 40%.

17. 100 c.c. of a mixture of CO, CH_4, and H_2 are mixed with 300 c.c. of O_2 and fired. After cooling the resulting gas occupied 285 c.c. and after absorption by potash 205 c.c. of O_2 remained. Find the composition of the mixture. CO 50 c.c.; CH_4 30 c.c.; H_2 20 c.c. *Calcutta* '41.

18. When 150 c.c. of ozonised oxygen were passed through a red-hot tube, 160 c.c. of gas remained. Calculate the composition of the original mixture. 13·33% ozone.

19. When 60 c.c. of a mixture of N_2O and NO were mixed with equal volume of pure hydrogen and exploded, 38 c.c. of pure N_2 were left. Calculate the quantity of each gas in the original mixture.
Allahabad '06. N_2O 16 c.c.; NO 44 c.c.

20. 36 c.c. of a mixture of methane, ethylene and acetylene were mixed with 100 c.c. of oxygen and sparked. The volume after explosion was 70 c.c. After absorption of CO_2 by KOH the volume was 10 c.c. Calculate the volume of each gas present. CH_4 12 c.c.; 12 c.c. C_2H_4; 12 c.c. C_2H_2.

21. 15 c.c. of carbon monoxide were mixed with 5 c.c. of oxygen and exploded. What is the volume and composition of the residual gas?
CO 5 c.c.; CO_2 10 c.c.

22. What volume of air at 27°C and 750 mm. would be required for the complete combustion of 100 c.c. of a gaseous mixture containing 46% H_2, 40% marsh gas and 14% CO by volume. Air contains 79% N_2 and 21 per cent O_2 by volume. *Calcutta* '21. 583·2 c.c.

23. 50 c.c. of a mixture of chlorine monoxide and chlorine dioxide are decomposed by a careful heating. The chlorine produced is absorbed by KOH solution and a diminution in volume of 40 c.c. resulted. Calculate the composition of the gaseous mixture of the oxides of chlorine.
Cl_2O 30 c.c.; ClO_2 20 c.c.

24. A mixture of 30 c.c. of nitrous oxide and another oxide of nitrogen was exploded with 60 c.c. of H_2. After explosion 45 c.c. of N_2 remained. The formula of nitrous oxide is N_2O; the second oxide of N, is 15 times heavier than hydrogen. Determine the formula of the oxide of nitrogen.
Nitric oxide, NO. *Patna* '37.

25. Two volumes of a certain gas when exploded with five volumes of oxygen yield exactly 4 volumes of CO_2 and 2 volumes of steam. 104 gms. of the gas occupy the same volume as 176 gms. of CO_2 measured under the same conditions. What is the gas? *Acetylene*, C_2H_2.

26. A fuel contains 90 p.c. carbon and 10 p.c. incombustible matter. What vol. of air at N.T.P. (containing 21% O_2 by vol.) will be required to completely burn one kilogram of this fuel? *Punjab* '39. 8000 litres.

27. A mixture of chlorine with an oxide of chlorine gave on explosion an expansion from 100 c.c. to 130 c.c. The exploded gas was found to contain 70 c.c. of chlorine and 60 c.c. of oxygen. What was the oxide, how much of it was there in the mixture? ClO_2; 60 c.c.

28. Assuming air contains 21% by volume of oxygen, what volume of air at 27°C and 750 mm. pressure will be required for the complete combustion of 60 gms. of a paraffin candle of 80% carbon and 20% hydrogen?
Calcutta '35. 831·2 litres.

29. Calculate the percentage composition by volume of a mixture of CO and CH_4, 105·5 c.c. of which required 90·4 c.c. of oxygen for complete combustion. *Calcutta* '49. CO 76·2%; CH_4 23·8%.

30. 5 c.c. of a mixture of methane and ethylene need 13·2 c.c. of oxygen. Find the volume of each present. 1·8 c.c. CH_4; 3·2 c.c. C_2H_4.

31. The gaseous product evolved on heating a mixture of oxalic and formic acids with conc. H_2SO_4, is led into caustic potash solution when the volume is decreased by one-sixth. Calculate the mols ratio of the organic acids in the mixture. 1 : 4

32. 9·3 c.c. of a gaseous hydrocarbon need for complete combustion 46·5 c.c. of oxygen, and gave 27·9 c.c. of carbon dioxide. What is the gas? C_3H_8.

33. A gaseous mixture of methane 40 c.c., carbon dioxide 25 c.c., hydrogen 35 c.c. is at N.T.P. Calculate the volume of oxygen at N.T.P. needed for its combustion. What would be the volume and composition of the final product at 0°C and 76 cm.? If the oxygen be obtained from potassium chlorate, what weight of this substance will be needed to produce it?
97·5 c.c. O_2; 65 c.c. CO_2; 0·36 gm.

34. On partly ozonising 100 c.c. of oxygen a decrease of 10 c.c. in volume resulted. What volume of ozone had been produced? The resulting gas was treated with an excess of potassium iodide solution. Calculate (a) what volume of gas would remain, (b) what weight of iodine would be liberated.
20 c.c. O_3; (a) 90 c.c.; (b) 0·2268 g. of I_2.

35. 45 c.c. of a hydrocarbon were mixed with 280 c.c. of oxygen and exploded in a cool eudiometer. The volume of the residual gas was 190 c.c. When caustic potash was added the volume decreased to 55 c.c. What is the hydrocarbon? C_3H_8

36. What volume of air containing 21 per cent of oxygen would be required for complete combustion of 15 litres of acetylene? 178·6 litres.

37. A metallic carbide was decomposed by water, evolving methane and hydrogen only. 1,000 c.c. of the gas evolved weighed 0·405 g.; 20 c.c. of the gas were exploded with 40 c.c. of oxygen. The residue on cooling occupied a volume of 25 c.c.; and of this 10 c.c. were absorbed by caustic potash. The remainder was absorbed by alkaline pyrogallate. What was the composition of the gas? CH_4 and H_2 in equal volumes.

38. A sample of water gas has the following composition 50% H_2, 48% CO, and 2% CO_2 by volume. 100 c.c. of water gas is mixed with 150 c.c. oxygen and the mixture sparked. Calculate the change in volume of gas mixture on cooling. 250 c.c. become 151 c.c.

39. What volume of oxygen would be required for the complete combustion of 250 c.c. of each of the following gases: (a) ethylene, (b) methane?
(a) 750 c.c.; (b) 500 c.c.

40. 5 c.c. of ethylene are mixed with 20 c.c. of oxygen and sparked. What is the composition by volume of the products of the reaction, all measurements are made above 100°C? 40% CO_2; 40% steam; 20 p.c. O_2.

41. A mixture of marsh gas and olefiant (C_2H_4) gas occupying 6·3 c.c. requires for its complete combustion 15·4 c.c. O_2 and produces 9·1 c.c. CO_2. Find the volume of each gas. CH_4 3·5 c.c.; C_2H_4 2·8 c.c.

42. A sample of coal gas contains 40 H_2, 35 CH_4, 15 CO and 10 C_2H_2; 100 vols. of this gas were exploded with 600 vols. of air (containing 21 p.c. O_2) in a eudiometer. Calculate the composition of the resulting mixture on cooling.
Punjab '49. N_2 86·58 p.c.; O_2 0·64 p.c.; CO_2 12·78 p.c.

43. 1 litre of a 3 : 2 mixture of water gas (H_2 50, CO 47, CO_2 3) and producer gas (N_2 60, CO 35, CO_2 5) is mixed with excess steam and passed over an iron oxide-catalyst. Find the nitrogen-hydrogen ratio in the resulting gases. 1 : 3.

44. 20 c.c. of a gaseous hydrocarbon were exploded with 66 c.c. of O_2. Residual gases after cooling occupied 56 c.c. On treatment with KOH the volume decreased to 16 c.c. The remaining gas was oxygen only. What is the gas? *Rajputana* '53. C_2H_2.

•

Volumetric analysis—Acidimetry and Alkalimetry

Neutralisation.— In neutralisation reactions, acids and bases react with each other in equivalent amounts producing salt and water (p. 131). In the following illustration a measured volume, say 25 c.c., of caustic soda solution is taken in a beaker—a drop of phenolphthalein solution is added to the solution, which is turned *pink* (phenolphthalein is *pink* in alkaline solution, and *colourless* both in neutral and acid solutions). Dilute hydrochloric acid is run into the solution drop by drop from a burette. As each drop of acid mixes with the alkali, the hydrogen ion of the acid reacts with the hydroxyl ion of the alkali, forming water. With the gradual addition of the acid, the hydroxyl ions, therefore, begin decreasing, until at a certain stage all the hydroxyl ions are used up. The solution is then said to the *neutral* and the process is known as *neutralisation.* The solution becomes *just* colourless at the *neutral point.* The volume of acid is then read from the burette; let it be 20 c.c.

∴ 25 c.c. of caustic soda solution = 20 c.c. of HCl solution.

Now, knowing the weight of caustic soda per c.c. of the solution, it is possible to calculate the weight of hydrochloric acid per c.c. of its solution from the relation :

$$HCl(36{\cdot}5) + NaOH(40) = NaCl + H_2O.$$

i.e., 36·5 gms. of hydrochloric acid are equivalent to 40 gms. of caustic soda in their power of neutralisation

Titration.—It is a process of volumetrically determining the unknown strength of a solution by reaction with a solution of known concentration (or what is called a *standard solution*) in presence of an indicator. In acidimetry the unknown strength of an acid solution is estimated by titration with a standard alkali solution. Alkalimetry is just the reverse process.

Let us take an example—25 c.c. of a 5 per cent caustic soda solution just neutralise 20 c.c. of a solution of hydrochloric acid. To find the strength of the acid :

25 c.c. of 5% NaOH solution contain 5/4 gms. of NaOH.

$$\underset{40}{NaOH} + \underset{36{\cdot}5}{HCl} = NaCl + H_2O.$$

i.e., 40 gms. of NaOH neutralise 36·5 gms. of HCl

∴ 5/4 gms. of NaOH neutralise (36·5/40)×5/4 or 1·14 gms. of HCl.

∴ 20 c.c. of HCl solution contain 1·14 gms. of HCl.

or 100 c.c. of HCl solution contain 5·7 gms. of HCl.

The strength of the acid is 5·7 per cent This is an example of acidimetry.

Neutralisation indicator.—An indicator is a substance (a weak organic acid or base) that has the property of changing colour when acid or base is added to it. When added to a liquid, it indicates by change of colour, if the liquid is acidic, neutral or alkaline; it is invariably used to indicate the end point of neutralisation of acids and alkalis during their titration. A good indicator should show *sharp contrast of colours* in solutions *just* acidic or alkaline. Litmus, methyl orange, methyl red, phenolphthalein, etc., are the indicators usually used. Litmus is a dye obtained from certain lichens.

Indicator	Colour in acid	Colour in alkali
Litmus	red	blue
Methyl orange	pink or red	yellow
Methyl red	red	yellow
Phenolphthalein	colourless	pink or red
Congo red	blue	red

of Indicators for neutralisation reactions depends on the strength of acids and bases (p. 131). HCl. H_2SO_4, HNO_3 are strong acids; oxalic acid and acetic acid are weak acids. NaOH and KOH are strong alkalis—NH_4OH is a weak base. Na_2CO_3 is the salt of weak carbonic acid.

Titration of	Indicator
(i) Strong acid—strong base	Any indicator
(ii) Strong acid—weak base	Methyl orange*
(iii) Weak acid—strong base	Phenolphthalein**

A weak acid is not titrated with a weak base, as no sharp end point is obtained.

* Methyl orange changes colour in fairly acid solution. The salt formed during neutralisation, e.g., $NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$, is hydrolysed giving a slightly acidic solution at the equivalence point (p. 134).

** Phenolphthalein becomes pink in fairly alkaline solution, as the salt formed during neutralisation, e.g., $CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$, is hydrolysed giving an alkaline solution at the end point. Methyl orange is the indicator in the titration of sodium carbonate with a strong acid, since the solution is acidic at the end point due to the displacement of carbonic acid.

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$$

But phenolphthalein becomes colourless (i.e., pink colour of Na_2CO_3 solution disappears) when only *half* of Na_2CO_3 is neutralised—at this stage Na_2CO_3 is converted into $NaHCO_3$ which is not alkaline to phenolphthalein.

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl.$$

So, at the neutralisation point, the acid poured is half the vol. actually required for

Standard solution.—A standard solution of a substance contains a known weight of it in a definite volume of the solution. Hence a standard solution is a solution of known strength, i.e., known concentration. The standard solution usually employed in titrations is the normal solution.

Normal solutions.—*A normal solution* of a substance contains one gram-equivalent of it per litre of the solution.

Equivalent weights.—The equivalent weight of an element has already been considered (p. 90). The equivalent weight of a compound is that weight of it which contains one gram equivalent weight of the component taking part in a reaction. With acids, the chief component is the replaceable hydrogen; with bases, it is the hydroxyl group, and with salts, it is generally the cation.

(i) The gram equivalent of an acid *is that weight of it which contains* 1·008 *grams of replaceable hydrogen* i.e., *which contains 1 atom of replaceable hydrogen.*

A normal solution is written as *N solution*, e.g., (N)HCl solution. Strengths of other solutions are expressed in terms of N solution; thus, solutions containing 1/2, 1/10th, 1/100th, twice or thrice the equivalent of a substance per litre are written as N/2 (semi-normal), N/10 (deci-normal), N/100 (centi-normal), 2N (twice normal) or 3N (thrice normal) respectively.

The number of replaceable hydrogen atoms in the molecule of an acid is its basicity (p. 132).

∴ **Gram-equivalent of an acid = its gram-molecular weight ÷ basicity.**

Acid	Mol. wt.	Basicity	Gram-equivalent
Hydrochloric, HCl	36·46	1	36·46
Nitric, HNO_3	63	1	63·0
Sulphuric, H_2SO_4	98	2	49
Oxalic acid, $C_2H_2O_4.2H_2O$	126	2	63
Phosphoric, H_3PO_4	98	3	32·67

Since 36·46 gms. of HCl = 22·4 litres of HCl gas at N.T.P., 22·4 litres of HCl at N.T.P. is also the equivalent of HCl.

(ii) **The gram-equivalent of a base** *is that weight of it which can neutralise one gram-equivalent of an acid,* i.e., *which reacts with 1·008 gms of replaceable hydrogen of an acid.*

One hydroxyl group reacts with one replaceable hydrogen atom, and hence the equivalent of a hydroxide = its molecular weight divided by the number of hydroxyl groups contained in its molecule.

$$NaOH + HCl \rightleftharpoons NaCl + H_2O\ ; \quad Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O.$$

One oxygen atom reacts with two hydrogen atoms, and hence the equivalent of a basic oxide = its molecular weight divided by *twice* the number of oxygen atoms contained in its molecule.

$$MgO + 2HCl = MgCl_2 + H_2O\ ; \quad Al_2O_3 + 6HCl = 2AlCl_3 + 3H_2O$$

The number of gram-equivalents of an acid which neutralises one gram-molecular weight of a base is the *acidity* (p. 132) of the base.

∴ **Gram-equivalent of a base = its gram-molecular weight ÷ acidity.**

Base	Mol. wt.	Acidity	Gram-equivalent
Caustic soda, $NaOH$	40	1	40
Caustic potash, KOH	56	1	56
Calcium hydroxide, $Ca(OH)_2$	74	2	37
Ammonia, NH_3	17	1	17
Ferric oxide, Fe_2O_3	160	6	26·67
Ferric hydroxide, $Fe(OH)_3$	107	3	35·67

17 gms. of NH_3 = 22·4 litres of NH_3 at N.T.P. = equivalent of NH_3.

(iii) **The gram-equivalent of a normal salt** *is that weight of it which contains one gram-equivalent of a metal (which is equivalent to 1·008 grams of hydrogen).* Since the gram-equivalent of a metal is the atomic weight divided by the valency, the equivalent of salt = its molecular weight divided by the *total valency* of the metal atoms contained in a molecule, i.e.,

$$\text{Gram-equivalent of a salt} = \frac{\text{gram molecular weight}}{\text{number of metal atoms} \times \text{its valency}}$$

equivalent × v = at wt = $\frac{\text{at wt}}{}$. = v

Salt	Mol. wt.	Total valency of metal	Eq. wt.
Sodium carbonate, Na_2CO_3	106	2	53
Calcium carbonate, $CaCO_3$	100	2	50
Ferric chloride, $FeCl_3,6H_2O$	270·5	3	90·17
Silver nitrate, $AgNO_3$	170	1	170
Silver chloride, $AgCl$	143·34	1	143·34
Copper sulphate, $CuSO_4,5H_2O$	249·5	2	124·75

In the case of salts which react with acids, such as carbonate, equivalents may also be determined with reference to the acids. The equivalent of the salt = its molecular weight divided by the number of equivalents of an acid with which one molecule of the salt reacts : thus,

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$$

One molecule of Na_2CO_3 reacts with 2 equivalents of HCl, and hence the equivalent of Na_2CO_3 = its mol. wt. ÷ 2 = 106 ÷ 2 = 53.

The equivalent weight of sodium bicarbonate, $NaHCO_3$, is its molecular weight which is 84, since it reacts with one equivalent of an acid :

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2$$

The equivalent of a compound, in general, is that weight of it which reacts with one equivalent of an element or compound whose equivalent is known; thus in $2NaOH + CO_2 = Na_2CO_3 + H_2O$.

2 equivalents of NaOH react with one molecule of CO_2.

$\therefore$ 1 equivalent of NaOH reacts with $\frac{1}{2}$ molecule of CO_2.

$\therefore$ the equivalent of CO_2 = mol. wt./2 = 44/2 = 22.

It must be clearly understood that the equivalent weight of a substance will depend upon the particular reaction in which it takes part.

A **molar solution** of a substance contains one gram-molecular weight (or one mole) of it per litre of the solution; thus a molar solution of H_2SO_4 contains 98 gms. of it per litre, but its normal solution contains only 49 gms. per litre.

Important principles in volumetric analysis.—(i) *Normality of a solution is equal to the number of gram equivalents of a solute per litre,* e.g., the normality of 0·4N NaOH solution is 0·4.

(a) $\textbf{Normality} = \dfrac{\textbf{weight of solute in grams per litre}}{\textbf{gram equivalent}}$

$\therefore$ (b) **Weight of solute in gram per litre = normality × gram equivalent.**

Thus, the weight of NaOH per litre of a 1·5N caustic soda solution = 1·5 × 40 = 60 gms.

Strength of a solution is usually expressed in terms of *normality* or *weight in grams per litre,* and sometimes in *percent strength,* e.g., a 2 p.c. NaOH solution means 2 gms. of NaOH per 100 c.c., or 10 × 2 gms., i.e. 10 × per cent strength per litre, and hence:

(c) $\textbf{Normality} = \dfrac{\textbf{10} \times \textbf{per cent strength}}{\textbf{gram equivalent}}$

Thus the normality of a 8 p.c. NaOH solution = 10 × 8/40 = 2N.

(ii) *Volume of a given solution is inversely proportional to its strength,* i.e., if the volume be increased the strength must be proportionately decreased, and *vice versa.*

Let the equivalent weight of a solute be p gms.

1000 c.c. of N solution of the solute contains p gms. of it.

or 1 c.c. of the N solution of the solute contain 0·00 p gm.

or xy c.c. of the N solution of the solute contains 0·00 $p \times xy$ gms.
Also, 1 c.c. of y (N) solution of the solute contains 0·00 py gms.

x c.c. of y (N) solution of the solute contains 0·00 $p \times xy$ gms.

∴ x c.c. of y (N) solution $= xy$ c.c. of (N) solution $=$ 0·00 $p \times xy$ gm. of solute.

i.e., **x c.c. of a y (N) solution = xy c.c. of a (N) solution.**

One equivalent of any acid can neutralise one equivalent of any base. Hence, solutions of acids and bases of the same strength must neutralise in equal volumes.

Let x c.c. of a y (N) acid solution neutralise p c.c. of a q (N) base solution.

Now, x c.c. y (N) acid solution $= xy$ c.c. of (N) acid solution
p c.c. of q (N) base solution $= pq$ c.c. of (N) base solution.

Since solutions of the *same* strength react in *equal* volumes xy c.c. must be equal to pq c.c.

i.e., **volume of an acid × its strength = vol. of a base × its strength.**

For two solutions which are equivalent :

volume × strength (solution I) = volume × strength (solution II).

(iv) **Reduction of strength by dilution.**—When a solution is *stronger* than the desired strength, it may be reduced to required strength by proper dilution.

Reduce to N/10 two hundred fifty (250) c.c. of 1·048 N/10 NaOH solution.
250 c.c. of 1·048 N/10 solution = 250 × 1·048 c.c. of N/10 solution.
= 262 c.c. of N/10 solution.

∴ to reduce the strength to *exactly* N/10 (262−250) or 12 c.c. of water are to be added to 250 c.c. of the solution.

Preparation of standard solution.—(i) To prepare 250 c.c. of N/10 sodium carbonate solution.—The gram equivalent of Na_2CO_3 is 53 gms., hence the requirement for 1 litre of N/10 solution = 5·3 gms., and that for 250 c.c. of N/10 solution = 5·3 ÷ 4 = 1·325 gms.

Some *pure* and *dry* sodium carbonate is taken in a weighing bottle; and about 1·325 gms. of it are *accurately weighed* out into a measuring flask of 250 c.c. capacity with the help of a chemical balance, and dissolved with distilled water—the volume of the solution is then made up to *just* 250 c.c. by gradual addition of water. The contents of the flask is well shaken to get a uniform solution.

Let the amount of sodium carbonate *actually* weighed = 1·3568 gms.
Now, 1·325 gms. per 250 c.c. of solution make just N/10 solution.

∴ ~~1·3568~~ gms. per 250 c.c. make (1·3568/1·325) N/10, i.e., 1·024 N/10 soln.

1·024 is called the *factor* of the solution.

Now, 250 c.c. of 1·024 N/10 Na_2CO_3 solution = 250 × 1·024 or 256 c.c. N/10 Na_2CO_3 solution.

Hence (256 − 250) or 6 c.c. of water are to be added to the solution to make it *exactly* N/10.

Factor.— Factor of a solution = weight *actually dissolved* ÷ the *theoretical weight* required to be dissolved to prepare a solution of given strength.

In the above example, 1·024 is the factor of the N/10 Na_2CO_3 solution and hence the strength of the solution = 1·024 N/10. i.e. factor × the normality of the soln. prepared

The strength of a given solution is usually expressed with a factor.

(i) To prepare approximately N/10 solution of sulphuric Acid.— The equivalent of sulphuric acid is 49 gms. and hence 1 litre of the N/10 solution will contain 4·9 gms. of the acid. But sulphuric acid is not weighed, since is it *highly hygroscopic* and is also *not cent per cent pure.* From the specific gravity and the purity of a sample of acid, the volume of it that will contain 4·9 gms. of real and *pure* sulphuric acid is calculated.

Let the specific gravity of a sample of sulphuric acid be 1·84 and its purity 95·6 per cent.

95·6 gms. of pure H_2SO_4 are present in 100 gms. of the sample of the acid.

∴ 4·9 gms. „ „ „ „ (100 × 4·9)/95·6 gm. of the acid.

Now, mass = volume × density; and hence the volume of the sample of acid required = weight of the acid divided by its density = (100 × 4·9/95·6) ÷ 1·84 = 2·8 c.c. nearly. Hence, about 2·8 c.c. of the sample of the acid is measured out by a pipette into a litre-measuring flask and diluted with water up to 1000 c.c. This is approximately N/10 sulphuric acid solution. Similarly, approximately standard solutions of HCl and HNO_3 can be prepared.

To prepare 1 litre of approximately (N) acid solution.

Let e = *equivalent weight of acid.*

p = purity, i.e., per cent strength by weight.

s = sp. gr. of a sample of acid.

v = volume of the acid to be diluted to 1 litre.

Then, $v = 100\ e/ps$.

Some typical volumetric analysis.—(i) To find the strength of an acid solution i.e., standardisation of an acid solution.— The strength of an acid solution is determined by titration against a standard solution of sodium carbonate which is directly prepared, since the sodium carbonate can be obtained very pure (p. 405) and accurately weighed easily. N/10 solutions are usually used in volumetric analysis.

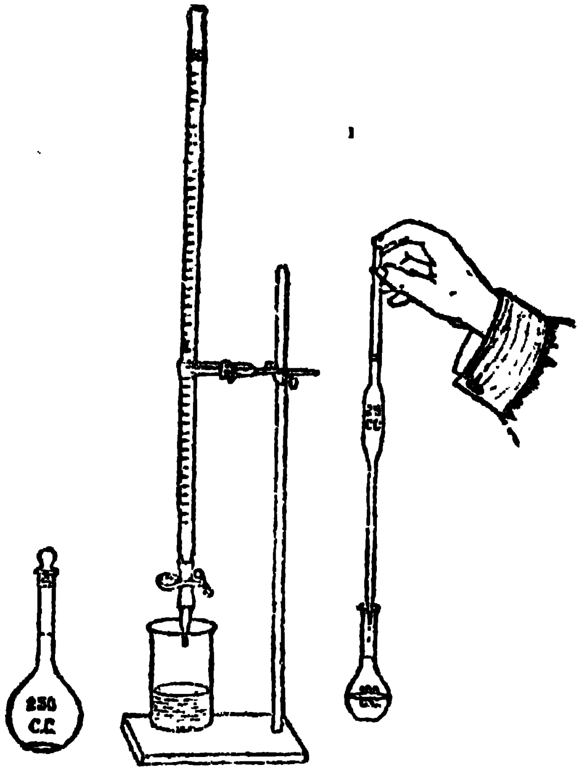
A burette (fig. 195) is filled with the approximately N/10 sulphuric acid solution up to the zero mark. 25 c.c. of N/10 sodium carbonate solution is taken in a basin by means of a pipette and diluted to about 50 c.c. with water—a drop of *methyl orange* solution (indicator) being added to the solution, which turns the solution *yellow*. The acid solution is gradually added drop by drop from the burette to the sodium carbonate solution until the *pink colour* is just obtained—the solution being carefully stirred with a glass rod during the titration.

The volume of the acid used up is read from the burette. Three titrations are usually done and the mean of three readings taken. Suppose

25 c.c. 1·024 N/10 Na_2CO_3 solution = 24 c.c. acid solution.

Let x = the strength of the acid solution.

$\therefore$ $24 \times x = 25 \times 1{\cdot}024$ (N/10), whence $x = 1{\cdot}067$ (N/10).



(ii) **To prepare approximate N/10 caustic soda solution and determine its strength.** Since caustic soda is hygroscopic, its standard solution cannot be prepared by weighing only. Equivalent weight of caustic soda is 40 gms.; and hence a deci-normal solution will contain 4 gms. of caustic soda per litre.

Approximately N/10 solution is prepared by dissolving about 4 gms. of caustic soda (usually a slight excess is used, since caustic soda is not generally of cent per cent purity), obtained by weighing in a rough balance, in a litre of water. The solution is then titrated against a standard acid solution and its strength determined.

25 c.c. of the alkali solution is taken in a basin by means of a pipette and diluted to about 100 c.c.—a drop of *phenolphthalein* is added to the solution: the solution turns *pink*. Standard acid solution is run dropwise from a burette, stirring the solution all the time till the solution is *just colourless*. Suppose:

25 c.c. NaOH solution = 20 c.c. 1·067 (N/10) acid solution.

$\therefore$ strength of NaOH solution = $(20 \times 1{\cdot}067/25)$.N/10 = 0·8536 (N/10).

(iii) **To determine the amount of total alkali in soda ash (calculated as Na_2O).**—About 1·5 gm. of the sample of soda ash is weighed out accurately and dissolved in distilled water in a measuring flask of 250 c.c. capacity, and the volume of the solution is made up to *the mark*—the contents of the flask is well shaken to get a uniform solution. 25 c.c. of the solution is taken and titrated with a standard (strength 1·067 N/10) sulphuric acid solution using methyl orange as an indicator.

Let the weight of soda ash taken = 1·5130 gm.

volume of the soda ash solution = 250 c.c.

Suppose 25 c.c. of soda ash soln. = 20 c.c. of 1·067 N/10 acid soln.

= $20 \times 0{\cdot}1067$ c.c. of N acid soln.

= 2·134 c.c. of N soda ash soln.

Now, 1 c.c. of (N) Na_2CO_3 solution contains 0·053 gm. of sodium carbonate, and the weight of Na_2O : weight of Na_2CO_3 = 62 : 106.

∴ wt. of Na_2O in 1 c.c. of (N)Na_2CO_3 = (0·053×62)/106 = 0·031 gm.

∴ **25 c.c. of soda ash soln. = 2·134×0·031 or 0·066 gm. of Na_2O.**

∴ 250 c.c. of soda ash soln = 0·66 gm. of Na_2O.

∴ **% of Na_2O in the sample of soda ash = (0·66×100)/1·513 or 43·61%.**

(iv) To determine the percentage of pure H_2SO_4 in a sample of brown oil of vitriol.

About 20 to 25 drops of the brown oil of vitriol (commercial sulphuric acid) are taken by means of a pipette into a clean weighing bottle which has been weighed previously. The bottle is weighed again. The acid is transferred completely into a 250 c.c. measuring flask by repeatedly washing the bottle with water. The volume of the solution is made up to the mark, and the flask is shaken to get a uniform solution.

The strength of the acid solution is then determined against a standard solution of sodium carbonate, *vide supra.*

Let the weight of the acid = 1·6497 gm.

Volume of acid solution = 250 c.c.

Let the strength of sodium carbonate = 1·024 (N/10).

Suppose 25 c.c. of Na_2CO_3 solution = 20·5 c.c. of the acid solution.

∴ 20·5 c.c. of the acid solution = 25 c.c. of 1·024 (N/10) Na_2CO_3 solution.
= (25×0·1024) c.c. of (N) Na_2CO_3 solution.
= 2·56 c.c. of (N) acid solution.

But 1 c.c. (N) H_2SO_4 solution = 0·049 gm. of H_2SO_4.

∴ 25 ~~20·5~~ c.c. of the acid solution = 2·56×0·049 gm. of H_2SO_4.

∴ 250 c.c. of the acid = (2·56×0·049×250)/20·5 or 1·495 gm. of H_2SO_4.

This amount of H_2SO_4 is contained in 1·6497 gm. of oil of vitriol taken.

∴ % of H_2SO_4 in the sample = (1·495×100)/1·6497 = 90·65.

Exercises

1. What weight of sodium carbonate is required to neutralise 50 c.c. of normal H_2SO_4? *Calcutta* '13.

50 c.c. of N.H_2SO_4 will be neutralised by 50 c.c. of N.Na_2CO_3 solution.

Now, 1000 c.c. of (N) Na_2CO_3 solution contain 53 gm. of Na_2CO_3.

∴ 50 c.c. ,, ,, ,, ,, 2·65 gm. of Na_2CO_3.

2. 25 c.c. of N/10 hydrochloric acid neutralised 21 c.c. of solution of sodium carbonate. How much water must be added to 1 litre of the latter in order to make it exactly decinormal?

21 c.c. of Na_2CO_3 solution = 25 c.c. of N/10 HCl solution.

∴ strength of Na_2CO_3 solution = (25/21) N/10 = 1·1905 (N/10).

∴ 1000 c.c. of 1·1905 (N/10) Na_2CO_3 solution = 1000×1·1905 or 1190·5 c.c. of (N/10) Na_2CO_3 solution.

∴ (1190·5−1000) or 190·5 c.c. of water are to be added to 1000 c.c. of the solution.

3. 20 c.c. of a N/10 solution of HNO_3 is neutralised by 22·5 c.c. of Na_2CO_3 solution. Calculate the strength of the carbonate solution in terms of normality and the weight of the carbonate per litre of the solution. *Calcutta* '16.

22·5 c.c. of Na_2CO_3 solution = 20 c.c. of 0·1 (N) HNO_3 solution.

$$\therefore \text{ Strength of } Na_2CO_3 \text{ solution} = \frac{\text{vol. of acid} \times \text{strength of acid}}{\text{volume of } Na_2CO_3 \text{ solution}}$$

$$= (20 \times 0{\cdot}1N)/22{\cdot}5 = 0{\cdot}089 \text{ N}$$

Now, 1000 c.c. (N) Na_2CO_3 solution contain 53 gm. of Na_2CO_3.

∴ 1000 c.c. of 0·089 (N) Na_2CO_3 contain 0·089×53 or 4·72 gm. Na_2CO_3.

4. To 50 c.c. of solution of HCl 25 c.c. of 0·82 N.NaOH solution were added. The excess of acid in the solution required 30 c.c. of 0·09 N.Na_2CO_3 solution for neutralisation. Required the normality of the acid solution, and the number of grams of HCl per litre of the solution. *Calcutta* '21.

25 c.c. of 0·82 (N) NaOH solution = 25×0·82 or 20·5 c.c. of (N) NaOH solution.

30 c.c. of 0·09 (N) Na_2CO_3 solution = 30×0·09 or 2·7 c.c. of (N) Na_2CO_3 solution.

Hence the mixture of alkalis = (20·5 + 2·7) or 23·2 c.c. of (N) solution.
Let the strength of HCl solution be x, and since
Volume of acid × its strength = vol. of alkali × its strength
$\therefore$ 50×x = 23·2 N $\therefore$ x = 0·464 N
Now, (N) HCl solution contains 36·5 gm. of HCl per litre.

$\therefore$ 0·464 (N) HCl solution contains 36·5×0·464 or 16·93 gms. of HCl per litre.

5. 2·95 gm. of a dibasic acid was dissolved in water and the solution diluted to 250 c.c.: 25 c.c. of this solution was neutralised by 25 c.c. of N/5 Na_2CO_3 solution. Calculate the eq. wt. and mol. wt. of the acid.

25 c.c. of diluted acid = 25 c.c. N/5 Na_2CO_3 solution.
$\therefore$ 250 c.c. of diluted acid = 50 c.c. N Na_2CO_3 solution = 50 c.c. of N acid.
$\therefore$ 50 c.c. N acid contain 2·95 gm. of acid.
or 1000 c.c. N acid contain 59 gm. of acid.
$\therefore$ eq. wt. of the acid = 59 gm. and mol. wt. = 59×2 = 118 gm.

6. A specimen of limestone contains 60% $CaCO_3$. Calculate the amount of stone which will be required to generate just sufficient CO_2 to convert 1 litre of N.NaOH solution into sodium carbonate. *Calcutta* '31.

1 litre of N.NaOH solution contains 40 gms. of NaOH.

$$\underset{80}{2NaOH} + \underset{44}{CO_2} = Na_2CO_3 + H_2O$$

i.e., 80 grms. of NaOH react with 44 gms. of CO_2
40 ,, ,, ,, ,, 22 ,, ,,

$$\text{Now, } \underset{100}{CaCO_3} = CaO + \underset{44}{CO_2}$$

i.e., 44 grms. of CO_2 are obtained from 100 grms. of $CaCO_3$.
$\therefore$ 22 gms. ,, ,, ,, ,, 50 gms. ,, ,,

But limestone contains only 60% $CaCO_3$; hence 50 gms. of $CaCO_3$ are present in (100×50)/60 or 83·3 gms. of limestone. $\therefore$ limestone required = 83·3 gms.

7. 100 gms. of hydrochloric acid solution of sp. gr. 1·17 contain 33·4 gm. HCl. How many litres of acid solution of this strength would be required to neutralise 5 litres of a solution of caustic soda containing 0·042 gm. of NaOH per c.c.?

1 c.c. of NaOH solution contains 0·042 gm. NaOH.
$\therefore$ 5 litres ,, ,, ,, 0·042×5000 or 210 gm. NaOH.

$$\text{Now, } \underset{40}{NaOH} + \underset{36\cdot5}{HCl} = NaCl + H_2O$$

i.e., 40 gms. NaOH neutralise 36·5 gms. of HCl.
$\therefore$ 210 gms. ,, ,, 191·625 gm. of HCl
But only 33·4 gm. of HCl are present in 100 gm. of HCl solution.
$\therefore$ 191·625 gm. HCl ,, ,, ,, 573·7 gm. HCl solution.

Now, since mass = volume × density, the volume of HCl solution required = 573·7 ÷ 1·17 = 490 c.c. or 0·49 litre.

8. A weighed amount of ammonium chloride was boiled with an excess of strong caustic soda solution and the liberated gas was absorbed by 100 c.c. of a solution containing 4·9 gm. of H_2SO_4; part of the acid was thus neutralised, and the excess acid could be neutralised by 50 c.c. of sodium carbonate solution

containing 2·65 gm. of Na_2CO_3. Calculate the amount of ammonium chloride originally taken.

Normality of a solution = wt. of the solute per litre/the eq. wt.
∴ strength of the H_2SO_4 solution = 4·9×10/49 = 1N.
Strength of the Na_2CO_3 solution = 2·65×20/53 = 1N.
50 c.c. N.Na_2CO_3 solution = 50 c.c. N.H_2SO_4 solution.
∴ (100−50) or 50 c.c. N.acid were used in absorbing NH_3.

Now, 50 c.c. N.acid solution = 50 c.c. N.NH_3 solution.
= 50 c.c. N.NH_4Cl solution.

$$NH_4Cl + NaOH = NaCl + H_2O + NH_3.$$

The eq. wt. of NH_4Cl = its mol. wt. = 53·5 gm.

∴ wt. of NH_4Cl originally taken = 50×0·0535 gm. = 2·675 gm.

9. 1·08 g. of NH_4Cl was boiled with 62 c.c. of (N/2) NaOH till free from ammonia. 44 c.c. of N/4 HCl were required for neutralising the excess of alkali in the mixture. Calculate percentage of ammonia in the salt. *Calcutta* 1935.

62 c.c. (N/2) NaOH solution = 31 c.c. (N) NaOH solution.

Excess alkali = 44 c.c. (N/4) HCl = 11 c.c. (N) HCl.
= 11 c.c. (N) NaOH solution.

∴ (31−11) or 20 c.c. (N) NaOH were used to displace NH_3.
20 c.c. (N) NaOH = 20 c.c. (N) NH_3 = 20×0·017 gm. NH_3.

$$\text{p.c. of } NH_3 \text{ in } NH_4Cl = \frac{20\times0{\cdot}017\times100}{1{\cdot}08} = 31{\cdot}48.$$

10. One gram of impure sodium carbonate is dissolved in water and the solution is made up to 250 c.c. To 50 c.c. of this solution 30·4 c.c. of 0·15 (N) HCl is added and the mixture requires for neutralisation 10 c.c. of 0·12 (N) NaOH solution. Determine the strength of impure Na_2CO_3 solution in terms of normality and also the % of pure sodium carbonate in the impure sample. *Calcutta* '23.

30·4 c.c. of 0·15 (N)HCl solution = 30·4×0·15 or 4·56 c.c. of (N)HCl.
10 c.c. of 0·12 (N) NaOH solution = 1·2 c.c. of (N) NaOH solution.
= 1·2 c.c. of (N) HCl solution.

Hence (4·56−1·2) or 3·36 c.c. of (N) HCl solution neutralise 50 c.c. of the sodium carbonate solution.

Let x be the strength of the Na_2CO_3 solution, then
$50x$ = 3·36N whence x = 0·0672N.

1 c.c. of (N) Na_2CO_3 solution contains 0·053 gm. Na_2CO_3.
∴ 1 c.c. of 0·0672N ,, ,, 0·053×0·0672 gm. Na_2CO_3.
∴ 250 c.c. of 0·0672N solution contains 0·053×0·0672×250 or 0·8904 gm. Na_2CO_3.
250 c.c. of the carbonate solution contains 1 gm. impure Na_2CO_3.

Hence, 1 gm. impure Na_2CO_3 contains 0·8904 gm. pure Na_2CO_3.
∴ 100 ,, ,, ,, ,, 89·04 gm. ,, ,,
∴ % of Na_2CO_3 in the impure sample = 89·04.

11. 584 c.c. of gaseous hydrochloric acid measured at N.T.P. were passed into a solution of KOH. After the reaction the solution still remained alkaline. To this was added 58 c.c. of 1·2 N H_2SO_4 when the solution was completely neutralised. Calculate the total quantity of alkali in the solution. *Calcutta* '40.

22400 c.c. of HCl gas at N.T.P. = 1000 c.c. of (N) HCl solution.
∴ 584 c.c. ,, ,, ,, ,, = 26 c.c. ,, ,, ,, ,,
Hence, the KOH soln. = 26 c.c. of (N) HCl+58 c.c. of 1·2 (N) H_2SO_4.
= 26 c.c. of (N) HCl+69·6 c.c. of (N) H_2SO_4.
= (26+69·6) or 95·6 c.c. of (N) acid solution.
= 95·6 c.c. of (N) KOH solution.

Now, 1 c.c. of (N) KOH solution contains 0·056 gm. KOH.

∴ 95·6 c.c. ,, ,, ,, ,, 95·6×0·056 or 5·3536 gm. KOH.
∴ total alkali in the solution = 5·3536 gm.

12. 2 gms. of a mixture of carbonate, bicarbonate and chloride of sodium gave on gentle heating till no further evolution of gas occurred, 62 c.c. of CO_2 at 26°C and 752 m.m. pressure. 1·6 gm. of the same mixture required 26 c.c. of (N) HCl for complete neutralisation. Calculate the percentage of carbonate, bicarbonate and chloride in the mixture. *Calcutta* '43.

Let the volume of CO_2 be v c.c. at N.T.P.

$\therefore$ $(v\times760/273 = (62\times752)/299.$ $\therefore$ $v = 56$ c.c.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

168 22400 c.c. at N.T.P.

i.e., 22400 c.c. CO_2 evolved on heating 168 gms. $NaHCO_3$

$\therefore$ 56 c.c. ,, ,, ,, ,, 0·42 gm. ,,

1·6 gm. of the mixture = 26 c.c. (N) HCl solution.

$\therefore$ 2 gm. ,, ,, ,, = 32·5 c.c. (N) HCl solution.

HCl neutralises both Na_2CO_3 and $NaHCO_3$ present in the mixture.

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2.$$

84 36·5

84 gms. $NaHCO_3$ = 36·5 gms. HCl, i.e., 1000 c.c. (N) HCl solution.

$\therefore$ 0·42 gm. $NaHCO_3$ = 5 c.c. of (N) HCl solution.

$\therefore$ the amount of Na_2CO_3 in the mixture = (32·5−5) or 27·5 c.c. (N) HCl.
= 27·5 c.c. (N) Na_2CO_3 solution.
= 27·5×0·053 or 1·457 gm. of Na_2CO_3.

$\therefore$ the amount of NaCl in the mixture = (2−0·42−1·457) = 0·123 gm.
Hence, in the mixture carbonate = (1·457×100) ÷ 2 = 72·85%;
bicarbonate = (0·42×100) ÷ 2 = 21·0%; chloride = (0·123×100) ÷ 2 = 6·15%.

13. 5 grams of sulphur were completely burnt in pure oxygen. Calculate the volume of the product measured at 25°C and 756 m.m. This amount of the gaseous product was led into 75 c.c. of a solution of caustic soda, which then required another 75 c.c. of the same solution to show a neutral reaction. Calculate the strength of caustic soda solution in terms of normality and also find the total quantity of solid present in the neutral solution. *Calcutta* '45.

$$S+O_2 = SO_2$$

32 22·4 litres at N.T.P.

$\therefore$ SO_2 produced = (22·4×5)/32 = 3·5 litres at N.T.P.

Let the volume at 25°C and 756 m.m. be v litres.

$\therefore$ (v×756)/298 = (3·5×760)/273, whence v = 3·84 litres.

$$SO_2 + 2NaOH = Na_2SO_3 + H_2O$$

22·4*l* 2×40 126

$\therefore$ 22·4*l* of SO_2 at N.T.P. = 80 gm. NaOH = 2000 c.c. (N) NaOH soln.
$\therefore$ 3·5 litres of SO_2 at N.T.P. = 312·5 c.c. (N) NaOH solution.
$\therefore$ (75+75) or 150 c.c. of the alkali solution = 312·5 c.c. (N) NaOH solution.
$\therefore$ the strength of the alkali solution = (312·5/150) N = 2·08N
Total solid in the solution = (126×3·5)/22·4 = 19·68 gms. of Na_2SO_3.

14. 1·5 gms. of a mixture of sodium carbonate and bicarbonate were dissolved in 250 c.c. of water. 25 c.c. of the solution required 27 c.c. of (N/10) HCl for neutralisation. Find the composition of the mixture.

Let the amount of sodium bicarbonate be x gms.

$\therefore$ 1000 c.c. of the solution contain 4x gms. $NaHCO_3$ and 4 (1·5−x) grams Na_2CO_3.

$\therefore$ the normality of $NaHCO_3$ in the solution=4x/84, the equivalent of $NaHCO_3$ being 84; the normality of Na_2CO_3 in the solution [illegible]x)/53.

$\therefore$ normality of the mixture = 4x/84+4(1·5−x)/53.

Now, 25 c.c. of the mixture = 27 c.c. of N/10 HCl solution.

$\therefore$ normality of the mixture = (2·7/25)N.

Hence 4x/84+4(1·5−x)/53 = 2·7/25, whence x = 0·187.

$\therefore$ amount of $NaHCO_3$ = 0·187 gm. and that of Na_2CO_3 = 1·313 gm.

Alternatively :

25 c.c. of the mixture = 27 c.c. N/10 HCl solution.
∴ 250 c.c. of the mixture = 27 c.c. NHCl solution.

Let the $NaHCO_3$ be x gm. ∴ the $Na_2CO_3 = (1{\cdot}5-x)$ gm.

$NaHCO_3 + HCl = NaCl + H_2O + CO_2$.
84 gm. 36·5 gm. or 1000 c.c. NHCl solution.
∴ x gm. of $NaHCO_3 = 1000x/84$ c.c. NHCl solution.

$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$.
106 gm. 2×36·5 or 2000 c.c. NHCl solution.
∴ $(1{\cdot}5-x)$ gm. of $Na_2CO_3 = 1000\,(1{\cdot}5-x)/53$ c.c. NHCl solution.
∴ total acid required $= 1000x/84+1000\,(1{\cdot}5-x)/53$.
∴ $1000x/84+1000\,(1{\cdot}5-x)/53 = 27$; whence $x = 0{\cdot}187$, etc.

15. 0·02 gm. of a metal after solution in water produced an alkali which was neutralised by 10 c.c. of N/10 HCl solution. Fin the eq. wt. of the metal.

10 c.c. N/10 HCl solution = 0·02 gm. of metal.
i.e., 1 c.c. NHCl solution = 0·02 gm. of metal.
∴ 1000 c.c. NHCl ,, = 20 gm. of metal.
∴ equivalent weight of the metal = 20.

16. 0·1232 gm. of a metal was dissolved in 50 c.c. N/2 HCl and the solution diluted to 100 c.c.; 20 c.c. of this solution was neutralised by 30 c.c. N/10 caustic soda. Calculate the eq. wt. of the metal.

20 c.c. diluted acid = 30 c.c. N/10 caustic soda.
100 c.c. diluted acid = 15 c.c. N caustic soda.
= 15 c.c. NHCl which was left unused.
Vol. of acid taken = 50 c.c. N/2 HCl. = 25 c.c. NHCl.
∴ Vol. of acid reacting with the metal = (25−15) or 10 c.c. NHCl.
i.e., 10 c.c. NHCl react with 0·1232 gm. of metal.
∴ 1000 c.c. ,, ,, ,, 12·32 gm. of metal.
∴ eq. wt. of metal = 12·32.

Exercises 15 and 16 illustrate methods of finding eq. wts. of metals by titration.

17. **Determination of mixed alkalis.**—To 20 c.c. of a mixture of NaOH and Na_2CO_3 are added a few drops of phenolphthalein and then on addition of 30 c.c. of N/10 HCl the pink colour just disappears. The same mixture is again titrated with the same acid after addition of methyl orange. 10 c.c. of the acid turns it pink. Calculate the amounts of NaOH and Na_2CO_3 per litre of the solution.

In the 1st titration phenolphthalein indicates the end point when all the NaOH and *half* of Na_2CO_3 only are neutralised—at this stage Na_2CO_3 being converted into $NaHCO_3$ which is not alkaline to phenolphthalein.

$$Na_2CO_3+HCl = NaHCO_3+NaCl.$$

In the 2nd titration methyl orange changes colour when all the $NaHCO_3$ (which is equal to half the sodium carbonate) is neutralised.

$$NaHCO_3+HCl = NaCl+H_2O+CO_2.$$

Hence volume of acid added in 1st titration = 30 c.c. of (N/10) HCl.
= all the NaOH + half the Na_2CO_3 of the mixture.
Volume of acid added in 2nd titration = 10 c.c. of (N/10) HCl.
= half the Na_2CO_3 in the mixture.
∴ the amount of NaOH in 20 cc. of the mixture.
= (30 [illegible]) c.c. of (N/10) HCl.
= 2 c.c. of (N) NaOH solution = 2×0·04 or 0·08 gm. of NaOH.
The amount of Na_2CO_3 in 20 c.c. of the mixture.
= twice the acid added in 2nd titration.
= 2×10 c.c. of N/10 HCl = 2 c.c. of (N) Na_2CO_3 solution.
= 2×0·053 or 0·106 gm. of Na_2CO_3.
∴ the amount of Na_2CO_3 per litre = 0·106×50 = 5·3 gm.

18. **To find the temporary hardness of water.**—100 c.c. of tap water was titrated with N/50 HCl with methyl orange as an indicator. If 30 c.c. of HCl were required, calculate the hardness as parts of $CaCO_3$ per 100,000 parts of water.

The reaction between calcium bicarbonate (temporary hardness) and HCl is :

$$Ca(HCO_3)_2 + 2HCl = CaCl_2 + 2H_2O + 2CO_2$$

∴ 2 equivalents of $HCl = Ca(HCO_3)_2 = CaCO_3$, since

$CaCO_3$ (100 parts)$+H_2O+CO_2 = Ca(HCO_3)_2$

∴ 1 equivalent of acid = 50 parts of $CaCO_3$

i.e., 1000 c.c. (N) acid = 50 gm. of $CaCO_3$.

or 1 c.c. (N) acid = 0·05 gm. of $CaCO_3$.

100 c.c. tap water = 30 c.c. N/50 HCl = 30/50 c.c. (N) HCl.

= (30/50)×0·05 or 0·03 gm. of $CaCO_3$.

∴ 100,000 c.c. tap water contain 30 gm. of $CaCO_3$.

19. **Precipitation method.**—A solution of silver nitrate may be used to determine the strength of chloride, bromide and iodide solutions.

25 c.c. of a solution containing KCl and NaCl were found to require 27·25 c.c. of 1·15 (N/10) $AgNO_3$ solution to precipitate all the chloride. Another 25 c.c. of the solution yielded a residue of 0·2088gm. Calculate the weight of KCl and NaCl present in a litre of the solution.

Let x gms. of NaCl be present in a litre of the solution, then (40×0·2088−x) = (8·352−x) gms. of KCl are present per litre.

∴ Normality of solution with respect to NaCl = x/eq. wt. of NaCl = x/58·5.

Normality with respect of KCl = (8·352−x)/74·5.

∴ total normality with respect to NaCl and KCl $= \frac{x}{58{\cdot}5} + \frac{8{\cdot}352-x}{74{\cdot}5}$

Now, 25 c.c. of solution of the mixed chloride = 27·25 c.c. of 1·15 (N/10) $AgNO_3$ solution.

∴ the normality of the solution = (27·25×0·115)/25N = 0·1254 N.

Hence $\frac{x}{58{\cdot}5} + \frac{8{\cdot}352-x}{74{\cdot}5} = 0{\cdot}1254$, whence x = 3·590

Weight of NaCl per litre = 3·590 gm.; weight of KCl per litre = 4·762 gm.

20. 55 c.c. of NaOH solution require 41 c.c. normal H_2SO_4 to neutralise it. Calculate the strength of alkali solution in terms of (a) normality, (b) percentage.
Andhra 1954. (a) 0·7454 N. (b) 2·98%.

21. 1·3456 gm. of Na_2CO_3 are dissolved in water and the volume of the solution made up to 250 c.c. 25 c.c. of this solution exactly neutralised 24·85 c.c. of a solution of H_2SO_4. Calculate the normality of (a) Na_2CO_3 solution, (b) acid solution, and the amount of Na_2SO_4 formed on neutralisation.
Calcutta '53. (a) 0·1016 N. (b) 0·1022 N; Na_2SO_4 0·1803 gm.

22. What weight of anhydrous sodium carbonate would be needed to prepare 500 c.c. of N/10 sodium carbonate solution. 2·65 gm.

23. In preparing a N/10 caustic soda solution about 4·4 gm. were weighed out and made up to 1 litre. 20 c.c. of this solution were neutralised by 22·2 c.c. N/10 HCl. How much water must be added to 250 c.c. of this caustic soda solution to make it exactly N/10? 27·5 c.c.

24. 5·3 gms. of moist sodium carbonate require 90 c.c. of a normal solution of acid to neutralise it. What is the percentage of water? 10 per cent.

25. The specific gravity of pure nitric acid is 1·522. What volume of such acid would be required to just neutralise 100 gms. of KOH? 73·9 c.c.

26. 22 c.c. of N/2 H_2SO_4 neutralised 20·6 c.c. of KOH solution. How much water must be added to 1 litre of the latter to make it exactly N/2?
68 c.c.

27. 0·4 g. of pure calcium carbonate was found to require 45 c.c. of dilute HCl for neutralisation. Calculate the normality of the acid.
Punjab 1942. 0·1778 N.

28. 2·25 gm. of a dibasic acid was dissolved in water and the solution diluted to 250 c.c. 25 c.c. of this solution required 40 c.c. of 1·25 N/10 alkali for neutralisation. Calculate the equivalent and molecular weights of the acid.
Eq. wt. 45; mol. wt. 90.

28a. What volume of normal sulphuric acid would be required to neutralise 5 litres of ammonia at 27°C and 750 mm. pressure? 2 litres.

29. 1·125 gm. of an acid (mol. wt. 90) was dissolved in 250 c.c. water; 25 c.c. of the solution were neutralised by 25 c.c. N/10 Na_2CO_3 solution. Find the eq. wt. and basicity of the acid. Eq. wt. 45; basicity 2.

30. What do you understand by a standard solution? How can you prepare a deci-normal solution of sulphuric acid?

Equal weights of NaOH and KOH are taken. Explain which would neutralise the larger quantity of an acid. Caustic soda.

A specimen of brown oil of vitriol had a density of 1·81 gm. per c.c. 10 c.c. of the acid was made to 1 litre with water. 10 c.c. of the solution required 28·8 c.c. of N/10 NaOH for neutralisation. Calculate the % of H_2SO_4 (by weight) in the commercial oil of vitriol. 77·94%.

31. What is meant by neutralisation? Why is a solution of sodium carbonate alkaline? Why must phenolphthalein not be used as an indicator for titration with sodium carbonate?

10 gms. of soda crystals ($Na_2CO_3,10H_2O$) are required to neutralise 50 c.c. of a sample of HCl solution. How many c c. of this acid must be diluted and made up to one litre so that we may get a N solution of HCl?
Calcutta '20. 715 c.c.

32. What volume of pure NH_3 at 27° and 750 mm. would be obtained from 10 gms. of NH_4Cl? What volume of N/10 H_2SO_4 would be neutralised by this ammonia. *Calcutta* '19. 4·661.; 1·87 litres.

33. SO_2 prepared by the action of excess strong H_2SO_4 upon 10 gms. of copper is passed through a litre of N/2 Na_2CO_3 solution. Find the weight of unchanged Na_2CO_3. (Cu=63). *Calcutta* '24. 9·7 gm.

34. 0·2815 gm. of $CaCO_3$ is dissolved in 30 c.c. (N) HNO_3. The excess of acid requires 24.43 c.c. of (N) NaOH. Calculate the percentage of CO_2 in the sample of $CaCO_3$. *Allahabad* '28. 43·53%.

35. 25 c.c. of an alkali solution is mixed with 8 c.c. of a 0·75 (N) acid solution and for complete neutralisation it further required 15 c.c. of a 0·8N acid solution. Find the strength of the given alkali solution.
Calcutta '30. 0·72 N.

36. A sample of dilute H_2SO_4, measuring 25 c.c. when treated with 1 gm. of $CaCO_3$ evolved 100 c.c. CO_2 measured at 20°C and 700 mm. Calculate the strength of the acid in gms. per litre and the amount of $CaCO_3$ remaining unchanged. *Allahabad* '27. 15 gm.; 0·617 gm.

37. 1·524 gms. of ammonium chloride were dissolved in water and 50 c.c. of (N) KOH solution were added to it. The total solution was boiled till ammonia ceased to be evolved, and was then neutralised with 30·95 c.c. (N) H_2SO_4 solution. Calculate the percentage of ammonia in the sample of ammonium chloride. *Calcutta* '31. 21·25%.

38. A solution contained sodium hydroxide and carbonate. Using phenolphthalein as indicator 25 c.c. of the solution required 17·8 c.c. N/10 HCl for neutralisation. Methyl orange was then added, when a further 15.7 c.c. of acid was required. Calculate the percentage of each constituent present in the mixture. Na_2CO_3 95·2%; NaOH 4·8%.

39. When a solution containing nitric and hydrochloric acids was treated with excess of silver nitrate, silver chloride was precipitated. It was found that 10 c.c. of the solution yielded 0·5 gm. silver chloride. 40 c.c. of this solution required 21 c.c. of (N) NaOH solution for neutralisation. Calculate the weights of nitric and hydrochloric acids present in a litre of the solution.
[Ag=108; Cl=35·5]. HNO_3 11·12 gm., HCl 12·73 gm.

40. 0·3363 gm. of a metal when added to 73 c.c. of distilled water produced 190 c.c. of hydrogen at 27°C and 720 m.m. and the solution became alkaline. Calculate the equivalent weight of the metal and the strength of the alkaline

solution in terms of normality. Guess what the metal is. 1*l.* of hydrogen at N.T.P. weighs 0·089 gm. Eq. wt. 23; 0·2 N; sodium. *Calcutta* '52.

41. What volume of N/10 HCl would completely dissolve 50 gms. of calcium carbonate. 10 litres.

42. Concentrated hydrochloric acid has a specific gravity 1·16 and contains 32 per cent of hydrogen chloride. Calculate the volume of this liquid which would be required to make ten litres of a normal solution of this acid. *Gauhati* '52; 983·3 c.c.

43. 25 c.c. of NaOH solution exactly neutralises 22·5 c.c. of solution (containing 1·4175 gm. in 250 c.c.) of a dibasic acid the molecular weight of which is 126, and 10 c.c. of the same NaOH solution also exactly neutralises 8 c.c. of a solution of H_2SO_4. Calculate the strength of the H_2SO_4 solution. Calcutta '29. 0·1013N.

✓ 44. 1 gm. of a mixture of sodium carbonate and bicarbonate was dissolved in 250 c.c. water. 25 c.c. of the solution required 15 c.c. of N/10 HCl for neutralisation. Find the percentage composition of the mixture. *Ans.* Na_2CO_3 44·45%; $NaHCO_3$ 55·55%.

45. 3·4914 gm. of a mixture of NaOH and KOH were made up to 250 c.c. 10 c.c. of this required for neutralisation 13·6 c.c. of 0·25 (N) HCl. Calculate the percentage of NaOH in the mixture. 90·83%.

46. 25 c.c. of a solution containing HCl and H_2SO_4 required for neutralisation 24·10 c.c. of N/2 NaOH solution. 25 c.c. of the solution on precipitation with barium chloride yield 0·5218 gm. of barium sulphate. What weight of each acid is contained in a litre of the solution.

[Ba = 137·5]. H_2SO_4 8·76 gm.; HCl 11·07 gm.

47. A specimen of chalk contained calcium sulphate as impurity. One gram of the solid was allowed to be in contact with 230 c.c. of N/10 HCl solution. The excess of acid in the mixture was completely neutralised by 8·0 c.c. of 0·45N NaOH solution. Calculate the percentage of chalk in the sample. *Calcutta* '43; 97%.

48 A solution contained sodium chloride and hydrochloric acid. 25 c.c. of the solution gave 1.792 gm. of silver chloride; if the molecular proportion of NaCl to the HCl is 3 to 1, calculate the normality of acid in the solution. [Ag = 108; Cl = 35.5]. 0·125N.

49. 75 c.c. of 0·2 N Na_2CO_3 were added to 50 c.c. of a solution of $Ba(NO_3)_2$ containing 0·034 gm. per c.c. The filtrate and washwater were made up to 250 c.c. 25 c.c. of this required for neutralisation 19·8 c.c. of 0·01 N HCl (factor 1·01). Find the percentage of barium in the compound. 52·523.

50. A standard potassium chloride solution is made by dissolving 8 gms. of the salt in a litre of solution. 25 c.c. of solution require 23·25 c.c. of a solution of silver nitrate to precipitate all the chloride as silver chloride. Calculate the normality of the silver nitrate solution. 0·1153 N.

51. 1·216 gm. of ammonium sulphate were boiled with an excess of caustic soda and the ammonia collected in 100 c.c. N.H_2SO_4. The partly neutralised acid was then titrated with N.NaOH solution and it required 81·6 c.c. of this solution to reach the end point. Calculate the percentage of ammonia in ammonium sulphate. *Punjab* '35; 25·72.

52. A solution contained sodium carbonate and bicarbonate. 25 c.c. of the solution required 5 c.c. of N/10 HCl for neutralisation, using phenolphthalein as indicator; methyl orange was then added, when a further 15 c.c. of acid was required. Calculate the amount of each salt in the given solution per litre. Na_2CO_3 2·12 gm; $NaHCO_3$ 3·36 gm.

53. A sample of KCl contains 1% NaCl. A solution of this salt is made containing 7·55 gm. of the impure chloride in a litre. Calculate the volume of N/10 $AgNO_3$ solution which is required to precipitate all the chloride contained in 25 c.c. of the solution. 25·4 c.c.

54. 16 gm. of a mixture of sodium sulphate and bisulphate was made up to 250 c.c. 10 c.c. of this require for neutralisation 8·4 c.c. of N/2 NaOH. Calculate the amount of sodium bisulphate. 12·6 gm.

55. 3·12 gm. of washing soda crystals were dissolved in 200 c.c. of water 20 c.c. of the resulting solution required 21·8 c.c. of N/10 H_2SO_4 for exact neutralisation. Calculate the percentage weight of anhydrous sodium carbonate in the crystals. 37·02.

56. 4·35 gms. of a mixture of NaCl and anhydrous Na_2CO_3 were dissolved in water and the solution made up to 100 c.c. 20 c.c. of the solution required 15·5 c.c. of N/2 H_2SO_4 to react completely with the sodium carbonate. Calculate the percentage composition of the original mixture.
NaCl, 52·8% ; Na_2CO_3 47·2%.

57. 1 gm. of a sample of dolomite containing $MgCO_3$ and $CaCO_3$ only was dissolved in 50 c.c. N/2 HCl solution; the excess acid was just neutralised by 18 c.c. N/10 NaOH solution. Find the percentage of $MgCO_3$ in the sample. 84 p.c.

58. 0·12 gm. of a metal dissolved completely in 25 c.c. N/2 HCl solution; the excess acid required 25 c.c. N/10 NaOH solution for neutralisation. Find the eq. wt. of the metal. 12

54. 1·054 gm. of a carbonate of a bivalent metal is dissolved in 50 c.c. N HCl and the excess of acid is neutralised by 25 c.c. N caustic soda. Find the eq. wt. and at. wt. of the metal. Eq. wt. 12·16; at. wt. 24·32.

60. 2·5 gms. of a mixture of NH_4Cl and NaCl are weighed out in a flask and 50 c.c. of solution of caustic soda (containing 24 gms. per litre) are added. The solution is boiled until all the ammonia has been expelled, and the excess of caustic soda is then titrated with 20·6 c.c. of a solution of sulphuric acid containing 38 gms. per litre. Calculate the % of NH_4Cl in the original mixture. 30% NH_4Cl.

61. 1 gm. of a mixture of sodium and potassium carbonate needs 19·7 c.c. of HCl containing 0·03 gm. of acid per c.c. What is the weight of each carbonate present? 0·612 gm. K_2CO_3; 0·388 gm. Na_2CO_3.

62. 0·21 gm. of a metal was treated with 100 c.c. N/2 H_2SO_4 till the metal dissolved completely. The residue required 32·5 c.c. of (N) NaOH solution for neutralisation. Calculate the equivalent of the metal. *Rajputana* '52. 12.

63. 500 c.c. of river water required 24 c.c. of N/10 H_2SO_4 using methyl orange. Calculate the temporary hardness in terms of $CaCO_3$ per 100,000 c.c. of water. 24 parts/100,000.

64. To find the permanent hardness in water; 20 c.c. were treated with 25 c.c. N/10 Na_2CO_3. The unused sodium carbonate was found to require 22·3 c.c. N/10 HCl. Find the hardness in terms of $CaCO_3$ per 100,000 c.c.
6·75/100,000.

65. 20 c.c. of a solution of H_2SO_4 neutralises 21·2 c.c. of a 3 per cent solution of Na_2CO_3. How would you reduce the strength of the acid to decinormal?
Strength = 0·6N. To every 1 c.c. of solution 5 c.c. of water.

66. Explain what do you understand by the normality of an acid or base. What is meant by neutralisation?

25 c.c. of solution of sulphuric acid neutralise 22·5 c.c.'s of a 4 per cent solution of sodium carbonate. How would you reduce the strength of the acid to decinormal? *Calcutta* '48. 1 litre to be diluted to 6·79 litres.

67. 7·5 g. of a dibasic acid are dissolved in water and the volume made up to 250 c.c. 25 c.c. of this acid solution require 16·1 c.c. of N NaOH for neutralisation. Find the molecular weight of the acid. 93·17.

68. To neutralise 10 c.c. of dilute hydrochloric acid 40 c.c. of normal sodium hydroxide were required. In another 10 c.c. of the same acid, 1 gram of precipitated chalk ($CaCO_3$) was dissolved, and it was then found that 20·5 c.c. of normal sodium hydroxide were required to neutralise the excess acid. Calculate the percentage of pure calcium carbonate in the precipitated chalk. 97·5%.

69. If 1 gm. of anhydrous sodium carbonate were added to 20 c.c. of a normal solution of sulphuric acid, what volume of CO_2 would be set free at N.T.P.? Would the resulting solution be acid or alkaline? What volume of N/10 acid or alkali would be required to neutralise it? *Ans. acidic;* alkali required = 11·3 c.c. of N/10 alkali; CO_2 formed 211·3 c.c.

70. When one litre of a solution of silver nitrate was electrolysed for sometime 0·1259 gm. of the metal was deposited on the cathode. 20 c.c. of the solution gave 1·667 gms. of silver chloride after electrolysis. Find the strength of the solution in terms of normality before and after electrolysis. Ag—108; Cl—35·5.
Calcutta, '57. 0·5821N before electrolysis; 0·5809N after electrolysis.

71. Explain what is meant by a normal solution. How does it differ from a 'molar' solution of a substance? What weight of sodium carbonate, sodium

bicarbonate and sulphuric acid will be required to prepare a normal solution of each?

Calculate the quantity of a sample of sodium carbonate, which contains 90 per cent carbonate and 10 per cent bicarbonate, that should be dissolved in water to make one litre solution, so that it will require an equal volume of N/5 sulphuric acid solution for complete neutralisation. *Calcutta* '50. 11·01 gm.

72. An excess of ferrous sulphide is added to 125 c.c. of dilute sulphuric acid and the volume of hydrogen sulphide set free measured 560 c.c. at 0°C and 760 m.m. Calculate the normality of the acid *Calcutta* '49. 0·4 N.

73. 2 gms. of the carbonate of a metal were dissolved in 50 c.c. (N)HCl solution. The resulting liquid required 100 c.c. N/10 NaOH solution to neutralise it completely. Calculate the equivalent weight of the carbonate.
Rajputana, '53. *Ans.* 50.

// 74. 10 c.c. of N sodium carbonate was required to neutralise 20 c.c. of a solution of sulphuric acid. What volume of gas would be obtained at N.T.P. by the action of 100 c.c. of this acid on zinc? *Calcutta* 1959; 0·56 litre.

Oxidation reactions.—*A normal solution of an oxidising agent, such as potassium permanganate or protassium dichromate, contains in 1 litre 1 gram-equivalent (8 gm.) of oxygen, available for oxidation.*

2 moles of potassium permanganate in acid solution give 5 atoms of available oxygen: $2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 3H_2O + 5O$. i.e., $2KMnO_4 = 5O = 10H$, $\therefore$ $KMnO_4/5 = H$ = equivalent weight.

$\therefore$ equivalent weight of $KMnO_4$ = mol. wt./5 = 158/5 = 31·6.

A normal solution of $KMnO_4$ contains 31·6 gms. of potassium permanganate per litre of the solution.

The equivalent of a substance depends upon the particular reaction in which it takes part, thus: ferrous salts are oxidised to ferric salts: $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$.

$\therefore$ $2KMnO_4 = 10FeSO_4$, i.e., $KMnO_4/5 = FeSO_4$ = eq. wt.

Hence the equivalent weight of ferrous sulphate is its molecular weight which contains 56 gms. of iron.

$\therefore$ *1 litre of N.$KMnO_4$ solution = 56 gm. of iron.*

Oxalic acid, $C_2H_2O_4$, is oxidised to carbon dioxide and water by $KMnO_4$ in hot dilute H_2SO_4 solution.

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_2 + 10CO_2 + 8H_2O.$$

$\therefore$ $2KMnO_4 = 5C_2H_2O_4.2H_2O$ (oxalic acid crystals contain 2 molecules of water of crystallisation).

$\therefore$ $KMnO_4/5 = C_2H_2O_4, 2H_2O/2$ = equivalent weight.

$\therefore$ the equivalent weight of oxalic acid crystals = 126/2 = 63.

Also, 1 litre of N.$KMnO_4$ solution = 63 gm. of oxalic acid crystals.

Potassium dichromate in acid solution yields 3 atoms of available oxygen: $K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$.

$\therefore$ $K_2Cr_2O_7 = 3O = 6H$, or $K_2Cr_2O_7/6 = H$ = eq. wt.

$\therefore$ equivalent weight of $K_2Cr_2O_7$ = mol. wt./6 = 294/6 = 49.

A normal solution of $K_2Cr_2O_7$ contains 49 gm. of potassium dichromate per litre.

Iodometry.— Iodine solution reacts with sodium thiosulphate $Na_2S_2O_3$; $2Na_2S_2O_3 + I_2 = Na_2S_4O_6$ (sodium tetrathionate) + 2NaI.

$\therefore$ $Na_2S_2O_3 = I = H$ = equivalent weight.

The equivalent weight of iodine is the same as its atomic weight, i.e., 127 mg. of iodine. From the reaction the equivalent weight of sodium thiosulphate is equal to its molecular weight.

A normal solution of iodine contains 127 gm. iodine per litre.

A normal solution of sodium thiosulphate contains 248 gm. of $Na_2S_2O_3, 5H_2O$ *crystals per litre.*

Consider the reaction: $2CuSO_4+4KI = 2CuI+I_2+2K_2SO_4$.

∴ $CuSO_4 = I = H$ = equivalent weight. The equivalent weight of copper sulphate in this reaction is its molecular weight which contains 63·54 gms. of copper.

∴ 1 litre of N. sodium thiosulphate solution = 63·54 gms. of copper.

Exercises

1. *0·7 gm. of oxalic acid crystals was dissolved in water, and the solution made up to 50 c.c. This solution required 11·1 c.c. of potassium permanganate solution for oxidation at 60°C. Calculate the strength of the latter.*

Equivalent weight of oxalic acid = 63 gms. 0·7 gm. of oxalic acid was dissolved in 50 c.c. ∴ 1000 c.c. of oxalic acid contained 14 gms. of the solid.

∴ the strength of oxalic acid = 14/63 N oxalic acid solution.

Now, 11·1 c.c. of $KMnO_4$ = 50 c.c. of the 14/63 N oxalic acid solution.

∴ strength of $KMnO_4$ = (50/11·1)×(14/63) N = 1·01 N.

2. *A solution of potassium dichromate was found to be* 1·035 N/10. *Calculate the volume of this solution which must be taken to make an exactly* N/10 *solution.* 23·35 *c.c. of this* 1·035 N/10 $K_2Cr_2O_7$ *solution oxidised 25 c.c. of a ferrous sulphate solution. Calculate the number of gms. of ferrous iron per litre of the solution.*

1 c.c. of 1·035 N/10 solution = 1·035 c.c. of N/10 solution.

∴ 1000 c.c. N/10 solution = 1000/1·035 or 966 c.c. of 1·035 N/10 solution, i.e., 966 c.c. of 1·035 N/10 solution are to be diluted to 1000 c.c. to make it exactly N/10.

25 c.c. of ferrous sulphate solution = 23·25 c.c. 1·035 N/10 $K_2Cr_2O_7$.

∴ strength of ferrous sulphate solution = (23·25/25)×(1·035/10)N = 0·096N.

∴ 1000 c.c. of 0·096 N ferrous sulphate = 0·096×56 or 5·4 gms. of iron.

3. *10 c.c. of a solution of hydrogen peroxide decolorised 50 c.c. of N/10 solution of acidified* $KMnO_4$. *What is the strength per litre of hydrogen peroxide?*

10 c.c. of H_2O_2 solution = 50 c.c. N/10 $KMnO_4$ solution

∴ strength of H_2O_2 = (50/10)×N/10 = N/2

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

∴ equivalent weight = $KMnO_4/5 = H_2O_2/2$

i.e., half the molecular weight of H_2O_2 is its equivalent weight = 17 gms.

1000 c.c. of N H_2O_2 solution = 17 gms. of H_2O_2

∴ 1000 c.c. of N/2 H_2O_2 solution = 8·5 gms. H_2O_2.

4. *A solution of a copper sulphate contains 25 gms. of the salt per litre of solution. 25 c.c. of a solution of 1·10 N/10 iodine solution reacts will 27·15 c.c. of a sodium thiosulphate solution. If 24·7 c.c. of this thiosulphate solution are required to reduce the iodine set free from 25 c.c. of the copper sulphate solution with potassium iodide, calculate the percentage of copper in the salt used.*

27·15 c.c. of thiosulphate solution = 25 c.c. of 1·1 N/10 iodine

∴ strength of thiosulphate = (25×1·1)/27·15.N/10 = 1·013 N/10.

Now, $2CuSO_4 + 4KI = 2CuI + 2K_2SO_4 + I_2$

∴ 1 equivalent of I_2 = 63·57 gms. of Cu = 1 equivalent of thiosulphate

1 c.c. of N/10 thiosulphate = 0·006357 gm. of copper

$\therefore$ 1 c.c. of 1·013 N/10 thiosulphate = 1·013×·006357 gm. of Cu

$\therefore$ 24·7 c.c. of „ „ = 1·013×·006357×24·7 gm. of Cu.
= 0·1591 gm. of Cu.

25 c.c. of copper salt contains 0·1591 gm. of Cu,

$\therefore$ 1000 c.c. of „ „ 0·1591×40 or 6·364 gms. of Cu.

i.e., 25 gms. of the copper salt contains 6·364 gms. of Cu

$\therefore$ the percentage of Cu = 6·364×4 = 25·456 gms.

---

5. What volume of a ferrous sulphate ($FeSO_4$) solution containing 16 g. per litre could be oxidised by 50 c.c. of N/10 permanganate? 47·5 c.c.

6. What weight of $KMnO_4$ would be needed to make 1 litre of the normal reagent (a) in acid solution, (b) in alkaline solution? 31·6; 52·7.

7. 25 c.c. of a solution of iodine of normality factor 0·115 requires 24·35 c.c. of a sodium thiosulphate solution for its reduction. Calculate the volume of this solution that must be taken to make one litre of just N/10 $Na_2S_2O_3$ solution. 847 c.c.

8. 11·380 gms. of bleaching powder were suspended in a litre of water. 25 c.c. of this suspension, on treatment with dilute HCl and potassium iodide liberated iodine, which required 24·37 c.c. of 0·1007 N sodium thiosulphate. What is the percentage of available chlorine in the bleaching powder? 30·61.

9. 0·29 gm. of a sample of pyrolusite, when warmed with strong hydrochloric acid, liberated chlorine which was equivalent to iodine contained in 61 c.c. of N/10 iodine solution. Calculate the percentage of manganese dioxide in the pyrolusite. 91·5 per cent.

10. 9·8 gms. of a ferrous compound were dissolved in sulphuric acid and diluted to 1000 c.c.; 4·5 c.c. of N/10 $K_2Cr_2O_7$ (factor = 0·8158) were required to completely oxidise 10 c.c. of the iron solution. Calculate the iron in the comfound. [Fe = 56]. 2 gm.

11. 0·806 gm. of a mixture of $KMnO_4$ and $K_2Cr_2O_7$ when dissolved in water and acidified was found to oxidise 50 c.c. of a solution of a ferrous salt containing 22·4 gms. of ferrous iron per litre. What is the composition of the mixture? 0·316 gm. of $KMnO_4$; 0·49 gm. of $K_2Cr_2O_7$.

12. What weight of chlorine would liberate a quantity of iodine from potassium iodide which would be exactly equivalent to 0·4 gm. of sodium thiosulphate crystals? 0·05725 gm. of chlorine.

13. What volume of N/20 $KMnO_4$ would oxidise 0·2 gm. of ferrous ammonium sulphate crystals? 10·2 c.c.

14. 1·12 gm. of a specimen of iron were dissolved in dilute H_2SO_4 and the solution made up to 200 c.c. 25 c.c. of this solution were oxidised by 24·8 c.c. of N/10 permanganate. Calculate the purity of the iron per cent. 99·2 per cent.

15. 1·2 gm. of commercial oxalic acid, $C_2H_2O_4$, $2H_2O$ were dissolved in 200 c.c. water. 10 c.c. of this solution required 8·5 c.c. N/10 $KMnO_4$ solution for complete oxidation. Calculate percentage purity of the sample.
Punjab 1949. 89·25 p.c.

APPENDIX

Balancing redox equations.—Redox equations involve simultaneous increase in valence (oxidation) of one element and decrease in valence (reduction) of another element. Such equations may be balanced by the valence number (also called oxidation number) method. The valence number of an element in a particular compound is a number which denotes the extent of oxidation or reduction necessary to change the element from the **free state** *into* that in the compound. The valence number is given a plus sign if oxidation is required to effect the change and a minus sign if reduction is necessary. The following rules apply in fixing valence numbers:—

(i) The valence number of an element in the free or uncombined state is zero.

(ii) In the combined state the valence number of:

(*a*) a hydrogen atom is +1, except in hydrides like NaH in which it is −1.

(*b*) an oxygen atom is −2, except in peroxides such as Na_2O_2 and H_2O_2 where it is −1.

(c) a metal atom is usually positive, except in certain hydrides, e.g., SbH_3, where it is negative.

(iii) The valence number of a radical or ion is that of its electrovalency.

(iv) The algebraic sum of the valence numbers of all the atoms in a compound is zero.

Illustrations.—The valence number of an atom of :

(*a*) carbon is +4 in $CO_2(2O=-4)$ and −4 in $CH_4(4H=+4)$.
(*b*) nitrogen is +5 in $HNO_3(3O=-6;\ H=+1)$ and −3 in $NH_3(3H=+3)$.
(*c*) sulphur is +6 in $H_2SO_4(4O=-8;\ 2H=+2)$ and −2 in $H_2S(2H=+2)$.
(*d*) chlorine is +7 in $HClO_4(4O=-8;\ H=+1)$ and −1 in $HCl(H=+1)$.
(*e*) manganese is +7 in $KMnO_4(4O=-8;\ K=+1)$ and +4 in $MnO_2(2O=-4)$.

For balancing redox equations : (i) write the formulæ correctly and indicate the valence numbers of those elements which change their valence in the reaction, e.g.,

$$\begin{array}{lcccc} & FeCl_3 + & SnCl_2 \longrightarrow & FeCl_2 + & SnCl_4. \\ \text{Valence numbers :} & +3 & +2 & +2 & +4 \end{array}$$

(ii) Make the increase in valence number for one element equal to the decrease in valence number for another, since oxidation must exactly compensate reduction, e.g.,

loss of 1 unit

$$FeCl_3 + SnCl_2 \longrightarrow FeCl_2 + SnCl_4.$$

gain of 2 units

To make the loss equal to the gain, the ratio of the oxidiser $FeCl_3$ to the reducer $SnCl_2$ must be 2 to 1.

(iii) Finally, balance the equation by inspection :

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

Illustrations.—(i) Action of hot concentrated sulphuric acid on carbon.

gain of 4 units

$$\begin{array}{ccccc} C\ + & H_2SO_4 \longrightarrow & CO_2\ + & SO_2\ + & H_2O. \\ 0 & +6 & +4 & +4 & \end{array} \qquad \text{(i)}$$

loss of 2 units

∴ proportion of C and H_2SO_4 must be 1 to 2.

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O. \qquad \text{(ii)}$$

(ii) Action of nitric acid (1 : 1) on copper.

gain of 2 units

$$\begin{array}{cccccc} Cu\ + & HNO_3\ + & HNO_3 \longrightarrow & Cu(NO_3)_2\ + & NO\ + & H_2O. \\ 0 & & +5 & +2 & +2 & \end{array} \qquad \text{(i)}$$

loss of 3 units

∴ proportion of oxidiser HNO_3 to reducer Cu must be 2 to 3.

salt former

$$3Cu + 6HNO_3 + 2HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O. \qquad \text{(ii)}$$

oxidiser

or $\mathrm{3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O}$. (iii)

(iii) Reduction of acidified potassium permanganate by nascent hydrogen.

—loss of 5 units per 1 Mn atom—

$$\underset{+7}{\mathrm{KMnO_4}} + \mathrm{H_2SO_4} + \underset{0}{\mathrm{H}} \longrightarrow \mathrm{K_2SO_4} + \underset{+2}{\mathrm{MnSO_4}} + \mathrm{H_2O} + \underset{+1}{\mathrm{H_2O}}. \tag{i}$$

——gain of 1 unit per H atom——

∴ ratio of $\mathrm{KMnO_4}$ to H atom must be 1 to 5.

$$\mathrm{KMnO_4 + H_2SO_4 + 5H \longrightarrow K_2SO_4 + MnSO_4 + H_2O + H_2O}. \tag{ii}$$

Multiplying by 2 and balancing the equation becomes

$$\mathrm{2KMnO_4 + 3H_2SO_4 + 10H = K_2SO_4 + 2MnSO_4 + 8H_2O}. \tag{iii}$$

(iv) Action of hot concentrated sulphuric acid on potassium iodide.

——gain of 1 unit per atom of I——

$$\underset{-1}{\mathrm{KI}} + \mathrm{H_2SO_4} + \underset{+6}{\mathrm{H_2SO_4}} \longrightarrow \mathrm{KHSO_4} + \underset{0}{\mathrm{I}} + \mathrm{H_2O} + \underset{+4}{\mathrm{SO_2}} \tag{i}$$

—loss of 2 units per atom of S—

∴ ratio of KI to oxidiser $\mathrm{H_2SO_4}$ must be 2 to 1

——salt former——

$$\therefore\ \mathrm{2KI + 2H_2SO_4 + H_2SO_4 \longrightarrow 2KHSO_4 + I_2 + 2H_2O + SO_2} \tag{ii}$$

——oxidiser——

or $\mathrm{2KI + 3H_2SO_4 = 2KHSO_4 + I_2 + 2H_2O + SO_2}$. (iii)

(v) Oxidation of ferrous sulphate by $\mathrm{KMnO_4}$ in sulphuric acid medium.

——loss of 5 units per Mn atom——

$$\underset{+7}{\mathrm{KMnO_4}} + \mathrm{H_2SO_4} + \underset{+2}{\mathrm{FeSO_4}} \longrightarrow \mathrm{K_2SO_4} + \underset{+2}{\mathrm{MnSO_4}} + \mathrm{H_2O} + \underset{+3}{\mathrm{Fe_2(SO_4)_3}}. \tag{i}$$

——gain of 1 unit per atom of Fe——

∴ ratio of $\mathrm{KMnO_4}$ to $\mathrm{FeSO_4}$ must be 1 to 5.

$$\mathrm{KMnO_4 + H_2SO_4 + 5FeSO_4 \longrightarrow K_2SO_4 + MnSO_4 + H_2O + Fe_2(SO_4)_3}. \tag{ii}$$

Multiplying by 2 and balancing, the equation becomes

$$\mathrm{2KMnO_4 + 8H_2SO_4 + 10FeSO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5Fe_2(SO_4)_3}. \tag{iii}$$

(vi) Action of hydrogen sulphide on sulphur dioxide.

gain of 2 units

$$\underset{-2}{\mathrm{H_2S}} + \underset{+4}{\mathrm{SO_2}} \longrightarrow \underset{0}{\mathrm{S}} + \mathrm{H_2O} + \underset{0}{\mathrm{S}}. \tag{i}$$

—loss of 4 units—

∴ ratio of reducer $\mathrm{H_2S}$ to oxidiser $\mathrm{SO_2}$ must be 2 to 1.

or $\mathrm{2H_2S + SO_2 = 2S + 2H_2O + S}$. (ii)

(vii) Action of dilute nitric acid upon tin.

——gain of 2 units——

$$\underset{0}{\mathrm{Sn}} + \mathrm{HNO_3} + \underset{+5}{\mathrm{HNO_3}} \longrightarrow \underset{+2}{\mathrm{Sn(NO_3)_2}} + \mathrm{H_2O} + \underset{-3}{\mathrm{NH_4NO_3}}. \tag{i}$$

salt former ——loss of 8 units——

∴ ratio of Sn to oxidiser $\mathrm{HNO_3}$ must be 4 to 1.

or $\mathrm{4Sn + 9HNO_3 + HNO_3 = 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3}$. (ii)

salt former oxidiser.

Measurements

The C. G. S. system.—The metric system is commonly adopted as the system of weights and measures in all scientific work. In this system, (i) the unit of length is the **centimetre,** (ii) the unit of mass is the **gramme,** and (iii) the unit of time is the **second.** Hence it is called **C.G.S.** or **centimetre-gramme-second system.**

The unit of length.— The *centimetre* (cm.) is one hundredth of a metre which is the exact distance between 2 marks on a standard bar of platinum at 0°C, preserved in Paris.

The unit of area.— The *square centimetre* (sq. cm.) is the area of a square of one centimetre side.

The unit of volume.— The *cubic centimetre* (c.c.) is the volume of a cube of one centimetre side. But the unit of volume or capacity often used is the *litre* which is *the volume of one kilogram of water at its maximum density at* 4°C. The litre was originally intended to be equal to 1 cubic decimetre, i.e., 1000 cubic centimetre. But 1 litre is nodw known to be equal to 1000·028 c.c. One *millilitre* (ml.) is one-thousandth of a litre, i.e., 1 ml. = 1·000028 c.c.

The unit of mass.—*Gram* or *gramme* is the mass of one cubic centimetre of water measured at 4°C, the temperature of maximum density. But this mass is now known to be 0·999,973 gram, i.e., 1 gram is the mass of 1·000028 c.c. of water at 4°C.

The unit of time.—The *second* is 1/86400th part of a mean solar day.

The normal or standard pressure.— This is defined as the pressure due to a column of mercury 76 cms. high at 0°C, at sea-level and latitude 45°, and is equal to $(76 \times 13{\cdot}596 \times 980)$ or $1{,}013 \times 10^3$ dynes per square centimetre (density of mercury = 13·596, and gravitational constant = 980) = 14·7 lbs. per sq. in.

In metric system the prefixes *deci- centi-* and *milli-* are used to denoto the fractions one-tenth, one hundredth, and one-thousandth, while the prefixes *deca-hecto-* and *kilo-* denote 10, 100, and 1000 times respectively.
1 metre (m.) = 10 decimetres = 100 centimetres (cm.) = 1000 millimetres (mm.)
1 gram (gm.) = 10 decigrams = 100 centigrams = 1000 milligrams (mg.)
1000 gms. = 100 decagrams = 10 hectograms = 1 kilogram (kg.)
1000 m. = 100 decametres = 10 hectometres = 1 kilometre (km.).

Conversion table of units

Length : 1 m. = 39·37 in. = 3·2809 ft. = 1·0936 yd.; 1 kilometre = 0·621 mile.
1 in. = 2·54 cm; 1 ft. = 30·48 cm.; 1 yd. = 0·9144 m.; 1 mile = 1·609 km.
Volume : 1 litre (*l.*) = 1000 millilitres (ml.) = 1000 c.c.; 1*l.* = 1·76 pint.
1 cu. in = 16·387 c.c.; 1 cu. ft. = 28·32 *l.*; 1 gallon = 4·546 litres.
1 gallon of water = 0·1605 cu. ft. = 4·546 *l.*; weighs 10 lbs.
1 cu. ft. of water at 62°F weighs 62·3 lbs.; 1*l* of water = 1000 c.c.; weighs 1 kg
Weight : 1 lb. = 16 oz. = 7000 grains = 453·59 gms. = 0·45359 kg.
1 kg. = 1000 gm. = 2·205 lbs. = 0·001 metric ton = 85·7 tolas.
1 gm. = 0·035 oz. = 15·43 grains; 1 oz. = 28·35 gm.; 1 grain = 0·065 gms.
1 tons = 27 maunds nearly; 1 stone = 14 lbs.
Apothecary's unit—1 c.c. = 0·033 ounce = 0·27 dram
1 ounce = 29·57 c.c.s; 1 dram = 3·7 c.c.s
Temperature—$°F = \frac{9}{5}°C + 32$; $°C = \frac{5}{9}(°F - 32)$.

Reactivity of metals

The following 12 metals (in the order of electro-chemical series, page 130) are considered.

Metal	Air (moist) at ordinary temp.	Air on heated metals.	Water	Non-oxidising acids HCl and dilute H_2SO_4		Oxidising acids Conc. H_2SO_4 and HNO_3			Alkali	Chlorine	Displacement.
K	K, Na and Ca tarnish—oxide film, finally hydroxide and carbonate.	K to Sn burn to K_2O_4 mainly	K, Na and Ca decompose cold water, liberating H_2.	Dilute HCl dissolves metals. K to Sn only (Sn only slowly liberating H_2.)	Dilute H_2SO_4 dissolves metals K to Sn only (except Al), liberating H_2.	Hot concentrated H_2SO_4 dissolves metals Mg to Ag, forming sulphate, water and sulphur dioxide.	Dilute HNO_3 dissolves all metals (except Al).	Conc. HNO_3 reacts with all metals (except Fe, Al & Pb).	Hot concentrated NaOH or KOH dissolves Al, Zn and Sn, liberating H_2.	Metals yield anhydrous chlorides, when heated in chlorine—Fe, Sn, Cu and Hg form -ic chlorides.	A metal higher up in the series displaces one below from its salt, e.g., $CuSO_4 + Fe = FeSO_4 + Cu$.
Na Ca Mg	tarnishes—oxide film.	Na_2O and Na_2O_2 CaO and Ca_3N_2 MgO and Mg_3N_2	Mg and Al amalgams and Zn-Cu couple decompose boiling water.				liberates H_2				
Al	protective oxide film.	Al_2O_3 and AlN					unattacked	scarcely attacked.			
Zn	basic carbonate film.	ZnO					forms NH_4NO_3				
Fe	reddish-brown rust.	Fe_3O_4 in O_2,	red hot Fe (also Mg and Zn) decomposes steam.	Hot conc. HCl reacts with all metals (except Hg and Ag), liberating H_2.			,,	becomes passive			
Sn	no action.	SnO_2 at white heat	no action.	readily dissolves			,,	deposits metastannic acid.			
Pb	basic carbonate film.	PbO and Pb_3O_4	corroded by water containing dissolved air.	reacts slowly				Pb scarcely attacked			
Cu	green basic sulphate film.	CuO	no action.	reacts slowly							
Hg	no action.	HgO (Pb, Cu & Hg do not burn).	no action.	no action.							
Ag	tarnishes—black sulphide film.	no action.	no action.	no action.							

ORGANIC CHEMISTRY

GENERAL THEORY

The growth of organic Chemistry.—Numerous natural products of plant or animal origin, e.g., oils, fats, gums, resins, sugars, starch, etc., had been known to the ancient people. Such common things as soap, dyes, drugs, wine, beer, perfumes and poisons, have been made since early times. The art of dyeing with indigo and alizarin is also a very old practice.

The next phase is marked by the isolation of many individual compounds. *Alcohol* was obtained very early by distillation of wine, and so also *acetic acid* by distillation of vinegar. Many acids were isolated from fruit and animal juices. *Formic acid* was prepared by distilling red ants in 1749. Towards the end of the 18th century Scheele isolated *citric acid* from lemon, *lactic acid* from sour milk, *oxalic acid* from wood sorrel, *gallic acid* from nut galls, *benzoic acid* from gum benzoin, and *tartaric acid* as the sour princippel of grapes. He also isolated *glycerine* from olive oil. In 1773 Rouelle isolated *urea* from human urine. *Morphine* was isolated from opium in 1805. The early chemists of the period also isolated the alkaloid drugs *quinine*, *cinchonine* and *strychnine*.

These and similar natural products were called **organic** to denote their origin from plant or animal sources, and were thus distinguished from inorganic substances such as acids, bases and salts, etc., which are made from lifeless rocks and minerals.

But beyond the separation of a number of natural products, nothing was known about their chemical nature. In 1874 Lavoisier showed by combustion analysis that *all* organic compounds consisted of *at least* carbon and hydrogen (hydrocarbons) and frequently oxygen (alcohol) and nitrogen (urea, morphine). Most of the organic compounds of diverse types and properties were soon found to be made of a few elements only, namely carbon, hydrogen, oxygen and nitrogen. Substances so unlike in properties as alochol, acetic acid, sugar, oils and glycerine, are made up of the *same* three elements carbon, hydrogen and oxygen in different proportions.

This was in sharp contrast to the inorganic compounds which were distinguished by their simplicity in composition. It was argued that such complexity in composition in organic compounds could be evolved out of a few elements only through the operation of a mysterious force *inherent in living cells;* this was called **vital force.** This led Berzelius to believe that organic compounds were produced under the influence of a vital force, and that they could not be prepared artificially. Organic substances could only be isolated as products of life processes.

This barrier of *vital force* which separated organic from inorganic chemistry was broken down in 1828, the year Wohler artificially prepared urea, a product of animal origin, by evaporating an aqueous solution of ammonium cyanate, an inorganic salt:

$$NH_4CNO \text{ (ammonium cyanate)} = CO(NH_2)_2 \text{ (urea)}$$

This was a direct refutation of the vital force theory, and in a letter to Berzelius he wrote, '*I must tell you that I can prepare urea without requiring a kidney or an animal, either man or dog.*' The synthesis of urea was followed by others, e.g., synthesis of acetic acid, and so the belief in vital force disappeared. It was soon realised that the same laws and the same forces operate in organic as in inorganic chemistry. So the terms organic and inorganic have lost their original meaning, and their retention is a matter of convenience. All the so-called organic compounds contain carbon, and since this is the one essential element, **organic chemistry may be defined as the chemistry of the carbon compounds.**

The elements commonly found in organic compounds are: carbon (always, by definition), hydrogen (almost always), oxygen, nitrogen, halogens, sulphur, phosphorus, and a few metals.

There are certain distinctive features of organic chemistry which justify its study as a separate branch of chemistry. The carbon compounds are far more numerous, about 10 lacs now, than the compounds of all the elements put together —the inorganic compounds total about 75 thousands only. The organic compounds are often very complex, as the following examples illustrate:

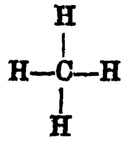
Cane sugar, $C_{12}H_{22}O_{11}$ Quinine, $C_{20}H_{24}O_2N_2$.

Carbon has the unique power to combine with other carbon atoms to form long chains. This largely explains the great complexity of organic compounds. The same formula may represent many different organic compounds. Thus the formula C_2H_6O stands for both ethyl alcohol and dimethyl ether. The same formula $C_{10}H_{18}O$ stands for 120 different compounds. But in inorganic chemistry a single formula stands for one compound only, e.g., H_2O stands for water only.

Organic compounds, with few exceptions, are combustible, while the inorganic substances as a rule do not burn. Unlike the inorganic compounds, the organic compounds usually melt at low temperatures and decompose at elevated temperatures. Organic compounds, as a rule, are soluble in organic solvents; few may dissolve in water, e.g., alcohol, acetic acid and sugar. Many inorganic compounds, on the other hand, dissolve in water, but not in organic solvents. Organic reactions are usually slow and are seldom quantitative, but the inorganic reactions are very quick and instantaneous. Organic compounds are mostly derived from coal tar, petroleum, and plant and animal sources. But an amazingly large number have also been synthesised in the laboratory. In this way many natural products have been produced artificially: notable examples are alizarin and indigo. Coal tar is a prolific source of organic compounds, and gave rise to the coal tar dye industry. It supplies practically all the dyes in use, and also many drugs, perfumes, flavours, developers and high explosives. Organic chemistry plays a great part in our daily life. Our foodstuffs, clothing, paper, plastics, dyes, drugs, hormones, vitamins, penicillin, petrol, rubber, etc., all are the gifts of organic chemistry.

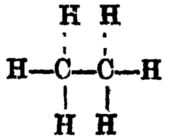
The linking of carbon atoms.—The valency of carbon, almost without exception, is four, and is conveniently represented by four bonds. The carbon atom and the simplest hydrocarbon methane are *graphically* written as follows:

Carbon atom



$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

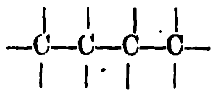
Methane, CH_4 .



$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C & -C & -H \\ & | & | & \\ & H & H & \end{array}$$

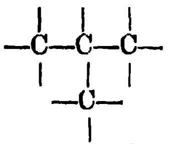
Ethane, C_2H_6

The carbon atom possesses the unique capacity for linking one to another to build up chains of carbon atoms—this property of carbon is known as *catenation.* The chain of carbon atoms may be open (straight or branched) or closed.

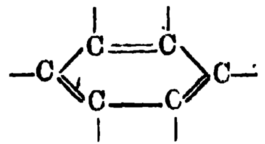


$$\begin{array}{ccccccccc} & | & & | & & | & & | & \\ - & C & - & C & - & C & - & C & - \\ & | & & | & & | & & | & \end{array}$$

Open chain (straight)

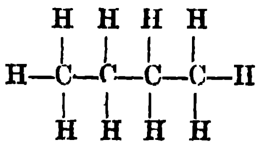


Open chain (branched)



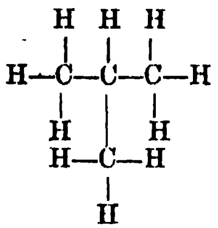
Closed chain

The skeletons of carbon chains such as the above are present in organic compounds. The unused valencies are then satisfied by atoms of hydrogen, oxygen, etc., according to the valency requirements of each carbon atom. When the valencies of the above carbon skeletons are satisfied by hydrogen, we get:

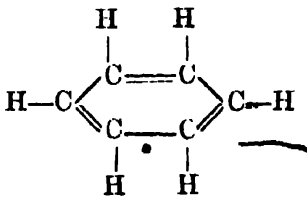


$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

Butane, C_4H_{10}



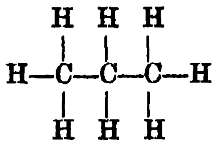
Isobutane, C_4H_{10}



Benzene, C_6H_6

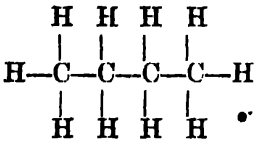
The *theory of carbon linkage*, based on the concept of catenation and quadrivalency of carbon, was developed by the famous German chemist Kekule in 1858. The theory clearly explains the structure of organic compounds.

The theory may be further explained with reference to hydrocarbons (i.e. compounds of carbon with hydrogen only). Two carbon atoms are linked together in ethane, C_2H_6. Similarly, chains of 3, 4 and 5 carbon atoms are present in propane, butane, and pentane respectively.



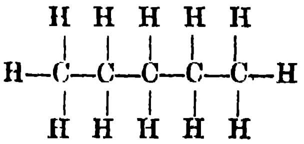
$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

Propane, C_3H_8



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

Butane, C_4H_{10}



$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

Pentane, C_5H_{12}

Methane is a saturated hydrocarbon, since all the valencies of carbon are fully satisfied. When all the valencies of carbon atoms in a chain are fully satisfied, the compound is said to be *saturated*, e.g., ethane, propane, butane. The carbon atoms are linked by *single bonds* in saturated compounds. When the valencies of carbon atoms in a chain are not fully satisfied, the compound is called *unsaturated.* In an unsaturated compound the adjacent carbon atoms may be linked by double bonds, as in ethylene, C_2H_4, and propylene, C_3H_6. The double bond is also called *ethylinic* or *olefinic linkage.*

$H_2C=CH_2$ Ethylene

$CH_3-CH=CH_2$ Propylene

An unsaturated compound may contain a *triple* bond (also called acetylinic linkage) between adjacent carbon atoms, as in acetylene and methyl acetylene.

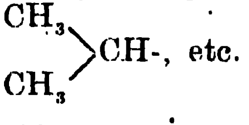
$H—C{\equiv}C—H$	$CH_3—C{\equiv}C—H$
Acetylene	Methyl acetylene

Homologous series.—The number of organic compounds is unbelievably large, but majority of them have been classified into several series of similar structure or constitution and chemical properties. Thus the hydrocarbons of the methane series, e.g., methane, ethane, propane, etc., form such a series, and is collectively known as *paraffins*. The paraffins may be given the general formula C_nH_{2n+2}. The molecular formula of each member of the series differs from that of another which precedes or follows it, by one atom of carbon and two atoms of hydrogen, i.e., by CH_2.

Paraffins, C_nH_{2n+2}		Alcohols, $C_nH_{2n+1}.OH$
Methane, CH_4		Methyl alcohol, CH_3OH
	: difference CH_2	
Ethane, C_2H_6		Ethyl alcohol, C_2H_5OH
	: difference CH_2	
Propane, C_3H_8		Propyl alcohol, C_3H_7OH
	: difference CH_2	
Butane, C_4H_{10}		Butyl alcohol, C_4H_9OH
	: difference CH_2	
Pentane, C_5H_{12} etc., etc.		Amyl alcohol, $C_5H_{11}OH$ etc., etc.

Such a series of organic compounds of similar structure (or constitution) and chemical properties, the successive member of which differs in molecular formula by CH_2 only, is called a *homologous series*, and the several members are known as homologues of one another.

Functional groups in organic chemistry.—Berzelius in 1817 recognised that organic compounds are made up of compound radicals —the radicals being linked to one another in the compounds. The structural formula of a given compound readily reveals the radicals present. Ethyl alcohol, $C_2H_5.OH$, for example, may be split up into ethyl, C_2H_5-, and hydroxyl, -OH, radicals. Similarly, acetic acid, $CH_3.COOH$, is made up of methyl, $-CH_3$, and carboxyl, -COOH, radicals. Such groups are called *compound radicals* or simply *radicals*.

The (aliphatic) hydrocarbon radicals are derived from corresponding paraffins and have a general formula C_nH_{2n+1}. A hydrocarbon radical, also called *alkyl radical*, contains one hydrogen atom less than a paraffin, and is monovalent, e.g., methyl, CH_3-, ethyl, CH_3-CH_2-, *n*-propyl, CH_3-CH_2-CH_2-, *iso*-propyl,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-$, etc.

The orderliness that we often come across in organic compounds is by and large due to the characteristic properties that a radical possesses. Hence in the study of organic compounds it is necessary to recognise the existence of principal radicals and know their properties. The consideration of a few homologous series will make things abundantly clear.

Alcohols, $C_nH_{2n+1}.OH$	Amines, $C_nH_{2n+1}.NH_2$
Methyl alcohol, $CH_3.OH$	Methyl amine, $CH_3.NH_2$
Ethyl alcohol, $C_2H_5.OH$	Ethylamine, $C_2H_5.NH_2$
Propyl alcohol, $C_3H_7.OH$	Propylamine, $C_3H_7.NH_2$
Butyl alcohol, $C_4H_9.OH$	Butylamine, $C_4H_9.NH_2$

Aldehydes, $C_nH_{2n+1}.CHO$	Acids, $C_nH_{2n+1}.COOH$
Formaldehyde, $H.CHO$	Formic acid, $H.COOH$
Acetaldehyde, $CH_3.CHO$	Acetic acid, $CH_3.COOH$
Propionaldehyde, $C_2H_5.CHO$	Propionic acid, $C_2H_5.COOH$
Butyraldehyde, $C_3H_7.CHO$	Butyric acid, $C_3H_7.COOH$

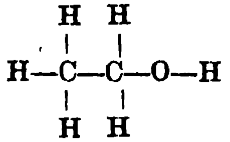
The chemical similarities in members of any particular series is due to some common radical in them, e.g., the properties of aldehydes are due to the presence of the aldehyde radical, $-CHO$; similarly the characteristic properties of alcohols depend on the hydroxyl radical, $-OH$. Such radicals as $-CHO$, $-OH$, $-COOH$, etc., upon which the characteristic properties of different classes of organic compounds largely depend are called **functional groups.** The properties of organic compounds are considered in terms of the radicals they are made up of. Hence it is in the fitness of things that organic compounds have been classified *according to the functional groups they contain.* Some of the principal types of organic compounds are:

Functional group	Class of compounds	Examples
Hydroxyl, $-OH$	Alcohols	Ethyl alcohol, $C_2H_5.OH$
Aldehyde, $-CHO$	Aldehydes	Acetaldehyde, $CH_3.CHO$
Keto, $-CO-$	Ketones	Acetone, $CH_3\text{-}CO\text{-}CH_3$
Carboxyl, $-COOH$	Acids	Acetic acid, $CH_3.COOH$
Amino, $-NH_2$	Amines	Methylamine, $CH_3.NH_2$
Amido, $-CONH_2$	Amides	Acetamide, $CH_3.CONH_2$

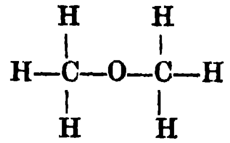
A few other commonly occurring functional groups are: *cyanide* (or nitrile), $-CN$, e.g., methyl cyanide, $CH_3.CN$; *acetyl*, CH_3CO-, e.g., acetyl chloride, CH_3COCl; *methylene*, $-CH_2-$, e.g., methylene chloride, CH_2Cl_2; *iminio*, $=NH$, e.g., dimethyl amine, $(CH_3)_2NH$; *nitro*, $-NO_2$, e.g., nitromethane, CH_3NO_2.

The functions of a given radical may be greatly influenced by its neighbours. The same bivalent *carbonyl group*, $>C=O$, for example, is present in (a) aldehydes as $\overset{H}{R—C}=O$, (b) ketones as $\overset{R}{\underset{R}{>}}C=O$, (c) acids as $\underset{OH}{R—C}=O$, and (d) amides as $\underset{NH_2}{R—C}=O$, where R is an alkyl radical (for ailphatic compounds).

[illegible]merism. —The same molecular formula may stand for different organic compounds. Thus the formula C_2H_6O represents both ethyl alcohol and dimethyl ether. (When two ~~or more~~ different compounds have the same molecular formula but differ in chemical and physical properties, they are said to be *isomers* of one another, and the phenomenon is known as *isomerism*:) *The isomers differ in structure or constitution*, i.e., in the arrangement of atoms within the molecule. The structural formulae of ethyl alcohol and dimethyl ether will make this clear :



Ethyl alcohol, CH_3CH_2OH



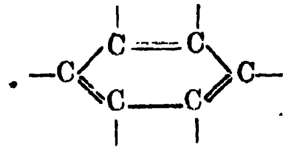
Dimethyl ether, CH_3-O-CH_3

The structural formula attempts to show the manner in which the radicals are combined in an organic compound.

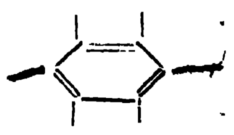
Divisions of organic chemistry.—There are three main divisions : *the aliphatic, the aromatic,* and *the heterocyclic compounds.*

The aliphatic compounds mostly contain *openchain of carbon atoms*, and are, therefore, called *open chain* or *acyclic compounds*. They got their name aliphatic from the fact that natural fats belong to this class. Methane, ethylene, $CH_2=CH_2$, acetylene, $CH\equiv CH$, ethyl alcohol, CH_3-CH_2OH, acetic acid, $CH_3.COOH$, etc., are aliphatic compounds.

The aromatic compounds are *closed chain* or *carbocyclic compounds*, and contain one or more six-carbon-atom benzene rings. The benzene ring is

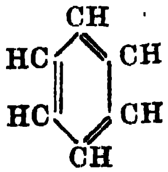


or briefly

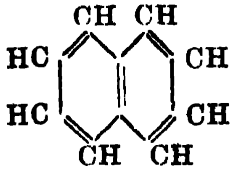


They are all related to the simplest aromatic compound benzene, C_6H_6, and many of them have sweet *aroma* or smell, and hence the name.

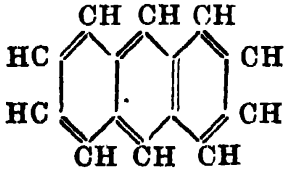
Naphthalene, $C_{10}H_8$, and anthracene, $C_{14}H_{10}$, are aromatic compounds.



Benzene, C_6H_6

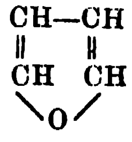


Naphthalene, $C_{10}H_8$

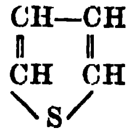


Anthracene, $C_{14}H_{10}$

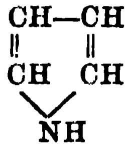
Heterocyclic compounds are also cyclic compounds, but the rings are not entirely carbocyclic (as in aromatic compounds) but contain atoms of elements besides carbon, e.g.,



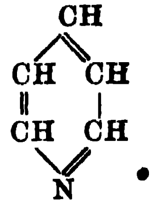
Furan



Thiophene

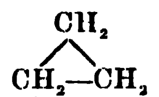


Pyrrole

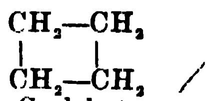


Pyridine

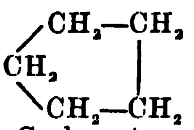
There is a group of carbocyclic or ring compounds which resemble aliphatic compounds in many ways ; they are known as *alicyclic* (aliphatic cyclic) compounds. The *naphthenes*, also called *cycloparaffins* or *polymethylenes*, are alicyclic compounds, e.g.



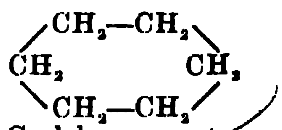
Cyclopropane



Cyclobutane



Cyclopentane



Cyclohexane

Organic compounds
- Open chain, aliphatic compounds, e.g. methane.
- Closed chain, or cyclic compounds
  - Homocyclic or carbocyclic compounds
    - Aromatic compounds, e.g., benzene
    - Alicyclic compounds e.g., cyclopropane.
  - Heterocyclic compounds, e.g., pyridine.

II

ALIPHATIC COMPOUNDS

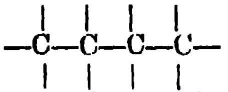
Paraffins

Paraffins.—The paraffins, also called **alkanes,** are saturated hydrocarbons (i.e. compounds composed of carbon and hydrogen only) —they form a homologous series of the general formula C_nH_{2n+2}. They are characteristically inert and hence the name '*paraffin*' hydrocarbons (Latin, *parum affinis*, little affinity).

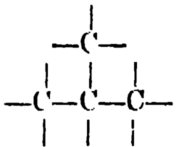
Paraffin	B.p.	Paraffin	B.p.
Methane, CH_4	−164°	Pentane, C_5H_{12}	36°
Ethane, C_2H_6	−90°	Hexane, C_6H_{14}	69°
Propane, C_3H_8	−38°	Heptane, C_7H_{16}	98°
Butane, C_4H_{10}	+1°	Octane, C_8H_{18}	125°
		etc., etc.	

The lower paraffins up to and including butane are gases, the members from pentane to pentadecane $C_{15}H_{32}$, are volatile liquids, and the still higher members of the series are solids.

Methane, CH_4, is a one carbon atom paraffin in which the valencies of carbon are fully satisfied by hydrogen. The carbon atoms of a paraffin are all linked to one another by *single bonds*, forming an open chain of carbon atoms (straight or branched), e.g.,



Straight chain



Branched chain

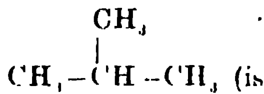
—the unused valencies of the carbon skeleton are fully satisfied by hydrogen, producing the saturated hydrocarbons (p. 3).

The molecular formula of the first three paraffins, namely methane, ethane, and propane, do not admit of more than one arrangement, and consequently they have no isomer.

CH_4 Methane $CH_3—CH_3$ Ethane $CH_3—CH_2—CH_3$ Propane

But butane and other higher paraffins exhibit the phenomenon of structural isomerism. Thus, the formula C_4H_{10} represents two isomeric paraffins, normal butane, b.p. +1°, and isobutane, b.p. —17°.

$CH_3-CH_2-CH_2-CH_3$ (n-butane)

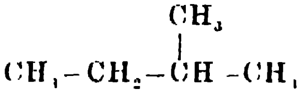


$CH_3-CH(CH_3)-CH_3$ (iso-butane)

There are three possible structures for pentane, C_5H_{12}, and three isomers exist.

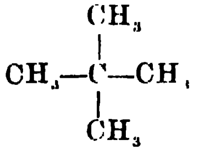
$CH_3-CH_2-CH_2-CH_2—CH_3$

Normal pentane, b.p. 38°



$CH_3-CH_2-CH(CH_3)-CH_3$

Isopentane, b.p. 30°.



$CH_3—C(CH_3)_2—CH_3$

Neopentane, b.p. 10°.

The number of possible isomers increases very rapidly with the increase of carbon atoms and there are as many as 75 alternative structures for decane $C_{10}H_{22}$.

Methane, also called *marsh gas*, CH_4 is the first member of the paraffin hydrocarbons. For its preparation, etc., see p. 330.

Ethane, C_2H_6, occurs in natural gas from petroleum wells, and also in coal gas. The paraffin next to methane is ethane and may be obtained by *similar* methods :

(i) By heating sodium propionate, CH_3CH_2COONa, with soda lime :

$$CH_3CH_2COONa + NaOH = CH_3\text{-}CH_3 + Na_2CO_3$$

(ii) By reducing ethyl iodide with nascent hydrogen from zinc-copper (or aluminium-mercury) couple and alcohol.

$$C_2H_5I + 2H = C_2H_6 + HI$$

(iii) **By Grignard's reaction.** —Ethyl iodide reacts with magnesium in dry ether medium, forming ethyl magnesium iodide, which is decomposed by water, giving ethane: $C_2H_5I + Mg = C_2H_5MgI$

$$C_2H_5MgI + H.OH = C_2H_6 + Mg(OH)I$$

(iv) Water acts on zinc ethyl, yielding ethane.

$$Zn(C_2H_5)_2+2H.OH = 2C_2H_6+Zn(OH)_2$$

Ethane is also obtained: (a) *by hydrogenation of ethylene* by passing a mixture of ethylene and hydrogen over finely divided nickel at 200-250°. (Sabetier and Sanderens method).

$$CH_2 = CH_2+H_2 \longrightarrow CH_3-CH_3$$

(b) **By Wurtz reaction** by the action of thin slices of metallic sodium upon methyl iodide (or bromide) in dry ether solution.

$$CH_3I+2Na+CH_3I \longrightarrow CH_3-CH_3+2NaI$$

(c) By the action of zinc upon methyl iodide.

$$2CH_3I+Zn \longrightarrow CH_3-CH_3+ZnI_2$$

Higher paraffins can thus be prepared by joining two alkyl groups by Wurtz reaction in which metallic sodium acts on an alkyl halide (or a mixture of 2 halides), usually a bromide or iodide, in dry ether solution. When a single alkyl halide is employed, a higher paraffin containing an *even* number of carbon atoms (which is double the carbon atoms of the alkyl halide) results, eg., ethyl iodide, C_2H_5I, gives normal butane, C_4H_{10}, by Wurtz reaction :

$$CH_3\text{-}CH_2I+2Na+CH_3\text{-}CH_2I \longrightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \text{ (n-butane)}+2NaI.$$

When, however, two different alkyl halides are used, a mixture of three paraffins is obtained, which is often difficult to separate. This limits the use of Wurtz' reaction. A mixture of methyl iodide and ethyl iodide, for example, produce ethane, propane and butane by the Wurtz reaction.

$$CH_3I+2Na+CH_3I \longrightarrow CH_3\text{-}CH_3 \text{ (ethane)}+2NaI$$

$$CH_3I+2Na+C_2H_5I \longrightarrow CH_3\text{-}CH_2\text{-}CH_3 \text{ (propane)} +2NaI$$

$$C_2H_5I+2Na+C_2H_5I \longrightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \text{ (butane)} +2NaI.$$

(d) **By Kolbe's synthesis.**—Electrolysis of an aqueous solution of sodium (or potassium) acetate liberates ethane and CO_2 at the anode, and caustic soda and hydrogen are formed at the cathode.

$$CH_3COONa \rightleftharpoons CH_3COO^-+Na^+ \text{ (in solution).}$$

$$2CH_3COO^- -2e = CH_3-CH_3+2CO_2 \text{ (at anode).}$$

$$2Na^+ +2e+2H_2O = 2NaOH+H_2 \text{ (at cathode).}$$

The above synthesis of ethane illustrate *general methods* of preparation of paraffins.

Ethane is a colourless gas (b.p. $-89°$), practically insoluble in water and slightly soluble in alcohol. It is very similar to methane in chemical properties. It is inflammable and burns with a feebly luminous flame and can be exploded with oxygen or air.

$$2C_2H_6+7O_2 = 4CO_2+6H_2O$$

It is a ***saturated*** hydrocarbon like methane, and ***cannot combine directly*** with chlorine or bromine. But like methane, it reacts with chlorine or bromine, giving a mixture of ***substitution products***, the hydrogens atom being replaced by chlorine or bromine in stages—the final products are C_2Cl_6 and C_2Br_6.

$$C_2H_6 \rightarrow C_2H_5Cl \rightarrow C_2H_4Cl_2 \text{-} \quad C_2H_3Cl_3 \text{ and so on.}$$

A résume of the methods of preparation of paraffins.—The starting materials are usually alcohols and acids : (i) *From alcohols.*—The alcohol is converted into an alkyl halide, usually a bromide (or iodide) by the action of red P and bromine (or iodine), e.g. $3C_2H_5OH + P + 3I \longrightarrow 3C_2H_5I$ (ethyl iodide) $+ H_3PO_3$.

The alkyl iodide is then converted into a paraffin :

(a) *by reduction with nascent hydrogen* : $C_2H_5I + 2H = C_2H_6 + HI$.

(b) *by Grignard reaction* : $C_2H_5I + Mg = C_2H_5MgI$.

$$C_2H_6MgI + H.OH = C_2H_6 + Mg(OH)I.$$

(c) *by Wurtz reaction* : $2CH_3I + 2Na = C_2H_6 + 2NaI$.

Besides, the alcohol may be dehydrated to an olefine by passing over heated alumina. The olefine is then reduced to a paraffin by catalytic hydrogenation.

$$CH_3.CH_2OH \text{ (ethyl alcohol)} \longrightarrow CH_2{=}CH_2 + H_2O$$

$$CH_2{=}CH_2 + H_2 \longrightarrow CH_3{-}CH_3.$$

(ii) *From fatty acids.*—(a) *by decarboxylation* of the sodium salt of the fatty acid by heating with soda lime : $CH_3{-}COONa + H.ONa \longrightarrow CH_4 + Na_2CO_3$.

(b) *by Kolbe's electrolytic method* by electrolysis of a solution of sodium (or potassium) salt of the acid, e.g., sodium acetate on electrolysis gives ethane (p. 9). When a mixture of two *different* salts is electrolysed, a mixture of *three* hydrocarbons is obtained. A mixture of sodium acetate and propionate on electrolysis gives ethane, C_2H_6, propane, C_3H_8, and butane, C_4H_{10}.

$$CH_3.COONa \rightleftharpoons CH_3.COO' + Na^+$$

$$CH_3\text{-}CH_2\text{-}COONa \text{ (sodium propionate)} \rightleftharpoons CH_3\text{-}CH_2\text{-}COO' + Na^+$$

At anode : $2CH_3COO' - 2e = C_2H_6$ (ethane) $+ 2CO_2$

$$2CH_3\text{-}CH_2\text{-}COO' - 2e = C_4H_{10} \text{ (butane)} + 2CO_2$$

$$CH_3COO' + CH_3\text{-}CH_2COO' \quad 2e = C_3H_8 \text{ (propane)} + 2CO_2.$$

At cathode : $2Na^+ + 2e + 2H_2O = 2NaOH + H_2$.

Petroleum.**—Petroleum (Latin, *petra*, rock ; *oleum*, oil ; literally means '*rock oil*') or *mineral oil* is the chief natural source of the paraffin hydrocarbons. The more important oil deposits occur in the U.S A., Mexico, Venezuela, U.S.S.R., Rumania, Iraq, Iran and Saudi Arabia. Small quantities are also found in Burma, and in Digboi in Assam. Recently a new oil field has been discovered in Nahorkatia in Assam. The crude petroleum is essentially a mixture of gaseous, liquid and solid hydrocarbons. The composition of oil from different oil fields may vary greatly but it always contains *some* of the paraffin hydrocarbons. The American oil consists chiefly of the paraffins. The oil beds generally lie at some distance, sometimes 1000-5000 ft., below the surface. The oil is raised by boring down to the oil-bearing strata and then pumping. Very often there is accumulation of ***natural gas under pressure in the oil field. The gas escapes during drilling or sometimes from a natural fissure. The '*eternal fire of Baku*' which attracted the fire-worshippers as early as 600 B.C., was due to the burning of natural gas from the oil fields. The natural gas contains gaseous paraffins, mainly methane. It may be used as a fuel.

The crude petroleum is a dark-brown viscous liquid. The crude oil is usually carried by iron pipe lines, some of which are 1700 miles long, to the sea-coast, and there fractionally distilled to separate the more volatile from the less volatile constituents. (Several commercially important fractions are collected. The lowest boiling fraction is **petroleum ether** (b. p. 40°—70°) and is used as a solvent for extraction of fats and oils, and in dry cleaning. **Petrol** or **gasoline** (b. p. 70°-120°) is a motor fuel. **Benzine** (b.p. 120°—150°) comes next, and is used as a solvent and also in dry cleaning. **Kerosene** (b.p. 150°—300°) is the next fraction and is the burning oil. The residual oil (m.p. above 300°) is the **crude oil** or **heavy oil.** It is used as a fuel oil. Steam ships and locomotives are often run with crude oil. Certain petroleum also gives **lubricating oil,** and **paraffin wax** (m.p. 45-65°) and **vaseline** (a lubricant and an ointment). Paraffin wax is used in making candles. The residue left in the still after distillation is the *pitch*. Pitch is used in road-making. Petroleum is the starting point for the preparation of many organic chemicals such as alcohol, acetone, glycerine, synthetic rubber and plastics.)

The kerosene oil for use in lamps should be free from too volatile paraffins, as shown by determination of its **'flash point',** otherwise serious explosions are likely to occur. (The flash point of the oil is a measure of its inflammability.)

***Cracking.**—There is a heavy demand for petrol for use as motor spirit. The demand is met by 'cracking' the heavy oil fraction of petroleum distillation. The heavy oil is a mixture of large hydrocarbon molecules of high boiling points. In this process the heavy oil is passed under pressure through a heated tube, often packed with a catalyst, when the large hydrocarbon molecules undergo thermal decomposition, producing a mixture of simpler molecules of low boiling points, which is used as petrol or *gasoline*. Many useful gases, e.g., ethylene, propylene, etc., are also formed during cracking.

Motor fuel from coal.—The production of synthetic liquid fuels, resembling petroleum, from coal is important in countries like India which do not possess large petroleum deposits. This is achieved by *hydrogenation* or *liquefaction of coal* by **Bergius process.** In this process coal dust is made into a paste with heavy oil and iron oxide catalyst and heated to 400-450°, and hydrogen is forced in under a pressure of 200 atmospheres, when the coal liquefies to a petroleum-like product. The product is distilled to give motor spirit (synthetic petrol), lubricating oil, and fuel oil. Motor fuel (synthetic petrol) is also made by **Fischer-Tropsch process** by passing a mixture of H_2 and CO (which may be made by passing steam over heated coke or coal) in the ratio of 2 :1 over a cobalt catalyst (containing thoria as promoter) at 200° under a pressure of 5-15 atmospheres.

Low temperature carbonisation of coal yields a tar which is rich in paraffin hydrocarbons. The low temperature tar on distillation also gives motor spirit.

The fossil fuels (coal and petroleum) in various forms are by far the most important sources of power. They two alone meet the major demand of our power requirements : coal and petroleum 80% ; wood, cowdung, and agricultural and forest products 15% ; hydro-electric power 1% ; the rest comes from miscellaneous sources, e.g., human and animal labour. But the fossil fuels will be exhausted within few generations. Hydro-electric power is a possible source. But it is available in certain regions only. Power from atomic fission is the only hope for the future. Power, therefore, poses a big industrial problem.

III

UNSATURATED HYDROCARBONS

The unsaturated hydrocarbons contain less hydrogen atoms than the paraffins with the same number of carbon atoms. There are not, therefore, enough hydrogen atoms in an unsaturated hydrocarbon to satisfy all the valencies of the carbon atoms. These hydrocarbons have the unique property of combining with other elements, e.g., chlorine and bromine, forming *additive compounds*, and are, therefore, called *unsaturated hydrocarbons*. The paraffins do not have this property and are called saturated hydrocarbons. In contrast to the paraffins, the unsaturated hydrocarbons are highly reactive.

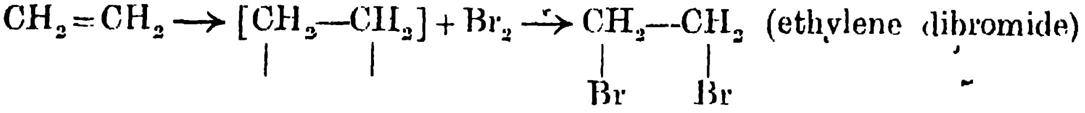
There are two important series of unsaturated hydrocarbons: (i) *the olefines*, and (ii) *the acetylenes*.

Olefines.—*The olefines*, also called **alkenes,** form a homologous series of unsaturated hydrocarbons of the general formula C_nH_{2n} (cf. paraffins C_nH_{2n+2}). (They contain *two* hydrogen atoms less than the corresponding paraffin, and possess a *double bond*, also called *olefinic linkage*,) between the two adjacent carbon atoms, e.g., $>C=<$. The first member of the series ethylnene, C_2H_4, contains 2 hydrogen atoms less than required to saturate the valencies of the 2 carbon atoms, and this is true of propylene, C_3H_6, butylene, C_4H_8, and the others.

Olefine (alkene)	Corresponding paraffin (alkane)
Ethylene, C_2H_4 $CH_2=CH_2$	Ethane, C_2H_6 $CH_3—CH_3$
Propylene, C_3H_6 $CH_3\text{-}CH=CH_2$	Propane, C_3H_8 $CH_3\text{-}CH_2\text{-}CH_3$

There is no one carbon member olefine corresponding to methane. The name of an olefine is derived from the corresponding paraffin by adding the termination *ylene* or *ene* for *ane*.

The important reactions of olefines are: (i) addition reactions.—The olefines readily form additive compounds—the double bond 'opens up' and the reagent such as bromine, etc., adds on the two active valencies:



$$CH_2=CH_2 \longrightarrow [\underset{|}{CH_2}—\underset{|}{CH_2}] + Br_2 \longrightarrow \underset{Br}{\underset{|}{CH_2}}—\underset{Br}{\underset{|}{CH_2}} \text{ (ethylene dibromide)}$$

The olefines readily react with:

(a) **Halogens.**—Halogens add to the double bond to give a *vicinal*-dihalide such as ethylene dibromide, $CH_2Br—CH_2Br$, as shown above.

Chlorine readily adds to a double bond , bromine is less reactive, but iodine does not add at all at ordinary temperature. Thus, ethylene readily adds chlorine or bromine, but not iodine.

The addition of bromine to a double bond is a general reaction and is used as a *test for unsaturation*. The reaction is carried out with a solution of bromine in chloroform or carbon tetrahcloride—the discharge of red colour due to bromine indicates unsaturation.

(b) **Hydrogen halides.**—Hydrogen halides add to the double bond in such a way that the hydrogen is added to one unsaturated carbon atom and the halogen to the other, e.g.,

$$CH_2 = CH_2 + HI \longrightarrow CH_3\text{-}CH_2I \text{ (ethyl iodide).}$$

The order of reactivity of the halides is opposite to that of the corresponding halogens, namely: HI > HBr > HCl.

Markownikoff's rule.—The addition of reagents like HBr, HI, HOCl and H_2SO_4, etc., to an *unsymmetrical* unsaturated hydrocarbon such as propylene, $CH_3\text{-}CH=CH_2$, is governed by Markownikoff's rule. It states that *the halogen atom or acid group* (*i.e., negative group*) *adds on the carbon atom which is linked to the least number of hydrogen atoms*, e.g.,

$$CH_3\text{-}CH = CH_2 + HI \longrightarrow CH_3\text{-}CHI\text{-}CH_3.$$

(c) **Sulphuric acid.**—The olefines add cold concentrated H_2SO_4 at the double bond, giving alkyl hydrogen sulphate—the product on hydrolysis gives alcohol:

$$CH_2 = CH_2 + H.HSO_4 \longrightarrow CH_3\text{-}CH_2\text{-}HSO_4 \text{ (ethyl hydrogen sulphate).}$$

$$CH_3\text{-}CH_2\text{-}HSO_4 + H.OH \longrightarrow CH_3\text{-}CH_2OH \text{ (ethyl alcohol)} + H_2SO_4.$$

The addition of H_2SO_4 to propylene follow Markownikoff's rule:

$$CH_3\text{-}CH = CH_2 + H.HSO_4 \longrightarrow CH_3\text{-}CH(HSO_4)\text{-}CH_3$$

$$CH_3CH(HSO_4)\text{-}CH_3 + H.OH \longrightarrow \underset{\text{Isopropyl alcohol}}{CH_3\text{-}CH(OH)\text{-}CH_3} + H_2SO_4$$

The net result of the addition of H_2SO_4 at the double bond and the hydrolysis of the product is the hydration of the double bond to give alcohols. The process is industrially important, as olefines, e.g., ethylene, propylene, etc., are by-products in cracking of petroleum.

(d) **Hypochlorous acid.**—Hypochlorous acid, HOCl, adds to the double bond to give chlorohydrins—hypochlorous acid acts as HO-Cl, and not as H-OCl.

$$CH_2 = CH_2 + HO\text{-}Cl \longrightarrow CH_2OH\text{-}CH_2Cl \text{ (ethylene chlorohydrin).}$$

(e) **Hydrogen.**—Olefines do not add hydrogen at the double bond in absence of a suitable catalyst. The double bond is conveniently reduced by treating the substance with gaseous hydrogen in presence of palladium, platinum black or nickel as catalysts, and the process is called *catalytic hydrogenation.*

$$CH_2 = CH_2 + H_2 \longrightarrow CH_3\text{-}CH_3 \text{ (ethane).}$$

Platinum and palladium are effective catalysts even at room temperature, but nickel requires a temperature in the region of 200° for effective hydrogenation.

Common reducing agents such as sodium and alcohol, metals and acids, sodium amalgam and aluminium amalgam, etc., are without effect on the double bond.

9 (ii) **Oxidation.**—In contrast to paraffins the olefines are sensitive to the action of oxidising agents. Even a mild oxidising agent like *cold and dilute alkaline* $KMnO_4$ solution oxidises an olefine, giving a *glycol*—the potassium permanganate solution is rapidly decolorised and a precipitate of manganese dioxide separates at the same time. *Baeyer's test* (p. 335) for unsaturation is based on the above reaction.

$$CH_2{=}CH_2+H_2O+O \longrightarrow CH_2OH\text{-}CH_2OH \text{ (ethylene glycol)}$$

$$3CH_2{=}CH_2+2KMnO_4+4H_2O \longrightarrow 3CH_2OH\text{-}CH_2OH+2KOH+2MnO_2.$$

But when the olefine is oxidised *without cooling* with alkaline permanganate or when it is oxidised with acidified permanganate or dichromate solution, the carbon linkage at the double bond gets severed, usually forming one or two molecules of organic acids, depending upon the position of the double bond— the lone carbon atom of a terminal double bond is, however, oxidised to CO_2.

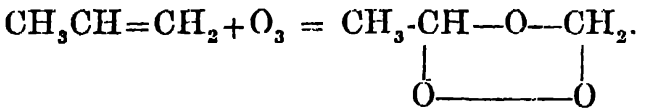
$$CH_2{=}CH_2+6,O = CO_2 + 2H_2O + CO_2$$

$$CH_3\text{-}CH{=}CH_2+5,O = CH_3COOH+CO_2+H_2O$$

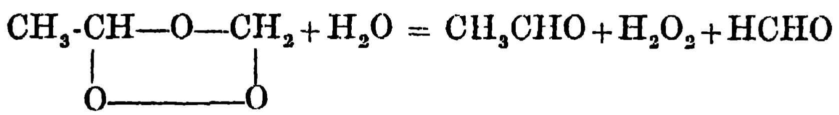
$$CH_3CH{=}CHCH_3+4,O = CH_3COOH+CH_3COOH$$

By identifying the products of oxidation the position of a double bond can be located.

9 (iii) **Ozonide formation.**—The action of ozone on olefines is more selective and is often used for the *detection and location of a double bond.* Ozone combines with olefines, forming ozonides (p. 334), which on decomposition with water (a process called **ozonolysis**) give a mixture of aldehydes (or ketones) and H_2O_2—the latter is destroyed by a mild reducing agent, e.g., zinc and water, as it may oxidise the aldehyde to an acid. By identifying the products of ozonolysis the position of a double bond is located: .



$$CH_3CH{=}CH_2+O_3 = \underbrace{CH_3\text{-}\overset{}{CH}\text{—O—}CH_2}_{O\text{———}O}.$$



$$\underbrace{CH_3\text{-}CH\text{—O—}CH_2}_{O\text{———}O}+H_2O = CH_3CHO+H_2O_2+HCHO$$

merisation.—One of the outstanding properties of olefines is the ness with which they undergo *polymerisation*—a process which in a broad sense means joining of several molecules to form a large one. Polymerisation can be effected merely by heating, but catalysts such as sulphuric acid and boron fluoride, are often used. Ethylene polymerises under a high pressure of 1000 atmospheres and at about 200°C to give the well-known *polythene* (or polyethylene) plastics.

$$CH_2{=}CH_2 + CH_2{=}CH_2, \text{ etc.} = (\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—})_n$$

9 **Preparation.**—The olefines are generally made: (i) by *dehydrating an alcohol* by passing its vapour over a heated alumina, e.g., propyl-alcohol, $CH_3CH_2CH_2OH$, gives propylene.

$$CH_3CH_2CH_2OH \longrightarrow CH_3CH{=}CH_2+H_2O$$

by heating an alkyl halide with an alcoholic solution of caustic potash, when a molecule of hydrogen halide is eliminated from the adjacent carbon atoms, producing a double bond, e.g., propyl iodide, $CH_3CH_2CH_2I$ gives propylene.

$$CH_3CH_2CH_2I + KOH \longrightarrow CH_3CH{=}CH_2 + KI + H_2O$$

Aqueous alkali is unsuitable, as the alkyl halide is insoluble in water. Alcohol dissolves the alkyl halide as well as the caustic potash, and hence the use of alcoholic potash. Besides, an alkyl halide is hydrolysed to an alcohol by aqueous alkali.

$$CH_3CH_2I + KOH\ \text{(aqueous)} \longrightarrow CH_3CH_2OH + KI$$
$$CH_3CH_2I + KOH\ \text{(alcoholic)} \longrightarrow CH_2{=}CH_2 + KI + H_2O$$

(iii) *by heating a vicinal-dihalide* in which the two halogen atoms are on adjacent carbon atoms (and hence in the same vicinity and so the name *vicinal-dihalide*) by zinc dust.

$$CH_2Br\text{-}CH_2Br + Zn \longrightarrow CH_2{=}CH_2 + ZnBr_2$$

The methods are in general available for the *introduction of a double bond in organic compounds.*

Ethylene, C_2H_4, is the first member of the olefine series. For its preparation, etc., see page 333.

The acetylenes

The **acetylenes,** also called **alkynes** or **alkines,** form a family of unsaturated hydrocarbons of the formula C_nH_{2n-2}. The simplest and the most important member is acetylene, C_2H_2. It contains 2 hydrogen atoms less than ethylene, C_2H_4, and bears the same relation to ethylene, as ethylne does to ethane, C_2H_6.

The acetylenes are named by changing the ending *ane* of paraffins to *yne* or *ine*. Thus :

$CH_3\text{-}CH_3$	$CH_2{=}CH_2$	$CH{\equiv}CH$
Ethane	Ethylene (ethene)	Acetylene (ethine)

The acetylenes contain a *triple bond* between adjacent carbon atoms, and are more unsaturated than the olefines. The acetylenes are usually obtained : (i) **by heating a vininal-dihalide with alcoholic potash,** e.g., $CH_2Br\text{-}CH_2Br + KOH \longrightarrow CH_2{=}CHBr + KBr + H_2O$

$$CH_2{=}CHBr + KOH \longrightarrow CH{\equiv}CH + KBr + H_2O$$

Vicinal-dihalides are readily obtained by the addition of halogens to olefines, e.g., $CH_2{=}CH_2 + Br_2 \longrightarrow CH_2Br\text{—}CH_2Br$ //

(ii) **by heating gem--dihalides** (in which the 2 halogen atoms are on the same carbon atom, and hence a *twinned* or *gem-dihalide*) **with an alcoholic solution of caustic potash,** e.g., ethylidene chloride, $CH_3\text{-}CHCl_2$, gives acetylene:

$$CH_3-CHCl_2 + KOH \longrightarrow CH_2{=}CHCl + KCl + H_2O$$
$$CH_2{=}CHCl + KOH \longrightarrow CH{\equiv}CH + KCl + H_2O$$

(iii) **by alkylation of acetylene.**—The hydrogen atom attached to a triply bound carbon atom, as in $CH{\equiv}CH$ and $CH_3.C{\equiv}CH$, has an acidic character, and is readily replaced by metals. Thus, sodium acetylide, $CH{\equiv}CNa$, is formed by the action of acetylene on a solution of sodium in liquid ammonia or by passing the gas into molten sodium at 180°. Disodium acetylide, $CNa{\equiv}CNa$, can be similarly obtained. $2CH{\equiv}CH + 2Na \longrightarrow 2CH{\equiv}CNa + H_2$.

The sodium acetylide reacts with methyl iodide, CH_3I, to give methyl acetylene, $CH_3\text{-}C{\equiv}CH$.

$$CH\equiv CNa + CH_3I \longrightarrow CH_3C\equiv CH + NaI.$$

Similarly, $CH_3\text{-}C\equiv CH + Na \longrightarrow CH_3\text{-}C\equiv C\text{-}Na + H$

$$CH_3\text{-}C\equiv C\text{-}Na + CH_3I \longrightarrow CH_3\text{-}C\equiv C\text{-}CH_3 + NaI.$$

Important reactions of acetylenes are: (i) **addition reactions.**—The acetylenes form *additive compounds* (p. 336) like olefines, but being more unsaturated, they enter into addition reactions more readily. The reaction takes place in two stages—an olefine being formed at the intermediate stage: $CH\equiv CH + H_2 \longrightarrow CH_2=CH_2$ (ethylene)

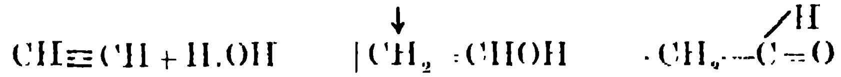
$$CH_2=CH_2 + H_2 \longrightarrow CH_3-CH_3 \text{ (ethane)}$$

The second addition of substances like HBr and HI, etc., follow Markownikoff's rule.

$$CH\equiv CH + HI \longrightarrow CH_2=CHI \text{ (vinyl iodide)}$$

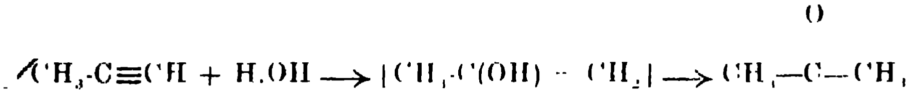
$$CH_2=CHI + HI \longrightarrow CH_3\text{-}CHI_2 \text{ (ethylidene iodide)}$$

(ii) **Hydration.**—Unlike the olefines which can be hydrated only by the indirect method of adding H_2SO_4 at the double bond and then hydrolysing the product (p. 13), *the acetylenes can be directly hydrated* in presence of mercuric sulphate catalyst in hot dilute sulphuric acid, e.g., acetylene on hydration gives acetaldehyde, $CH_3\text{-}CHO$ —the initial product being unstable vinyl alcohol, $CH_2=CHOH$, which is at once changed into acetaldehyde:



$$CH\equiv CH + H.OH \quad [CH_2=CHOH] \quad CH_3-\overset{H}{C}=O$$

Methyl acetylene, $CH_3\text{-}C\equiv CH$, on hydration gives acetone, $CH_3\text{-}CO\text{-}CH_3$ the initial addition follows Markownikoff's rule :



$$CH_3\text{-}C\equiv CH + H.OH \longrightarrow [CH_3\text{-}C(OH)=CH_2] \longrightarrow CH_3-\overset{O}{C}-CH_3$$

(iii) **Acetylides.**—Unlike the paraffins and olefines, the hydrogen of acetylene, $CH\equiv CH$, and the members of acetylene series, such as $CH_3\text{-}C\equiv CH$, *which contain the grouping* $—C\equiv CH$, is readily replaced by metals, giving metallic derivatives, called *acetylides*. Thus when shaken with ammoniacal cuprous chloride or silver nitrate solution, acetylene gives a precipitate of cuprous or silver acetylide (p. 337).

$$HC\equiv CH + 2CuCl \longrightarrow CuC\equiv CCu + 2HCl$$

$$HC\equiv CH + 2AgNO_3 \longrightarrow AgC\equiv CAg + 2HNO_3$$

The acetylides regenerate acetylene on treatment with dilute acids.

$$AgC\equiv CAg + 2HNO_3 \longrightarrow HC\equiv CH + 2AgNO_3$$

The acetylinic hydrocarbons which do not contain the unit $\equiv CH$, such as $CH_3\text{-}C\equiv C\text{-}CH_3$, do not form acetylides. The reaction is specific to hydrocarbons *containing acetylinic hydrogen*, (i.e., the unit $\equiv CH$), and hence can be used as a test for the recognition of compounds containing the unit $\equiv CH$.

(iv) **Polymerisation.**—Acetylene can be polymerised to benzene by the application of heat (p. 337). By absorption of acetylene in a solution of cuprous chloride and ammonium chloride in hydrochloric acid, the dimer vinyl acetylene is obtained—a key intermediate for making the synthetic rubber, *neoprene*.

$$CH\equiv CH + CH\equiv CH \longrightarrow CH_2=CH—C\equiv CH \text{ (vinyl acetylene).}$$

Acetylene, C_2H_2.—Acetylene is the simplest and the most important member of the series of alkines. For its preparation etc., see page 335. It is a cheap raw material for the industrial synthesis of important organic compounds.

Detection of unsaturation.—The presence of unsaturation in an unsaturated hydrocarbon is readily detected by its decolorisation of (i) bromine water or (ii) cold dilute alkaline potassium permanganate solution (*Bayer's test*).

IV

HALOGEN DERIVATIVES OF PARAFFINS

Monohalogen derivatives.—The monohalogen derivative of a paraffin (i.e., a paraffin in which one of the hydrogen atoms is replaced by a halogen) is called an **alkyl halide.** It has the general formula $C_nH_{2n+1}.X$, where X is a halogen atom, e.g., Cl, Br and I, and C_nH_{2n+1} **an alkyl group.** The alkyl group is monovalent and contains one hydrogen atom less than a paraffin.

The alkyl halide takes its name from the corresponding paraffin, the ending *-ane* being replaced by *-yl*. The following will make this clear.

Paraffin C_nH_{2n+2}	*Alkyl group* C_nH_{n+1}	*Alkyl halide* $C_nH_{2n+1}X$
Methane CH_4	Methyl group CH_3	Methyl chloride CH_3Cl
Ethane C_2H_6	Ethyl ,, C_2H_5	Ethyl bromide C_2H_5Br
Propane C_3H_8	Propyl ,, C_3H_7	Propyl iodide C_3H_7I
Alkane RH	Alkyl ,, R	Alkyl halide RX

Methods of preparation.—(i) By direct halogenation of paraffins. Alkyl chloride or bromide is formed by the direct action of chlorine or bromine upon a paraffin in presence of sunlight (i.e., by substitution) —the result is invariably a mixture of substitution products, of which the simplest is the alkyl chloride or bromide. Thus, the action of chlorine on methane gives a mixture of substitution products, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 (p. 332).

The method, is, therefore, seldom used for the preparation of alkyl halides. Iodine can be directly substituted into a paraffin only *in presence of iodic acid, HIO_3, or mercuric oxide, HgO,* which oxidises the HI formed back into iodine, otherwise the HI would reduce the alkyl iodide into the original paraffin. $CH_4+I_2 \rightleftharpoons CH_3I+HI$.

(ii) By passing HCl, HBr or HI gas into hot alcohol in presence of dehydrating agent, such as anhydrous zinc chloride, e.g.,

$$C_2H_5OH+HCl \rightleftharpoons C_2H_5Cl+H_2O$$

The reaction is reversible. The presence of zinc chloride prevents the back reaction by absorbing the water formed.

Alternatively, the alcohol may be heated with a potassium halide and excess of conc. H_2SO_4, e.g.,

$$C_2H_5OH + KBr + H_2SO_4 = C_2H_5Br+KHSO_4+H_2O$$

The excess sulphuric acid removes the water formed.

(iii) **By the action of halogen acids,** e.g., HI, HBr, etc., **upon an olefine :** $CH_2=CH_2+HI \longrightarrow CH_3\text{-}CH_2I$

(iv) **By the action of phosphorus halides upon an alcohol :**

$$3C_2H_5OH+PCl_3 = 3C_2H_5Cl+H_3PO_3$$

$$C_2H_5OH+PCl_5 = C_2H_5Cl+POCl_3+HCl$$

To obtain an alkyl bromide or iodide, it is convenient to prepare the phosphorus halide *in situ*, by treating the alcohol with red phosphorus and bromine (or iodine). The PBr_3 or PI_3 first formed reacts with the alcohol: $2P+3Br_2 = 2PBr_3$; $2P+3I_2 = 2PI_3$

$$3C_2H_5OH+PBr_3 = 3C_2H_5Br+H_3PO_3$$

$$3C_2H_5OH+PI_3 = 3C_2H_5I+H_3PO_3$$

Alkyl chlorides may be conveniently made, using thionyl chloride, $SOCl_2$ e.g., $C_2H_5OH+SOCl_2 = C_2H_5Cl+SO_2+HCl$

√ 9. **Preparation of ethyl bromide.**—10 gm. of red phosphorus and 70 c.c. of anhydrous ethyl alcohol are taken in a distilling flask (fig. 1) fitted with a tap funnel and attached to a condenser and receiver. The receiver is connected to a sodalime tower for absorbing HBr fumes. 20 c.c. of bromine is slowly run in from the tap funnel, while cooling the flask in water. The flask is allowed to stand for some hours, and the tap-funnel is replaced by a thermometer, and then its contents distilled from a waterbath until oily drops cease to collect in the reeciver. The distillate up to 60° is collected. It contains ethyl bromide. It is shaken several times with *sodium carbonate* solution to remove the alcohol (which dissolves in water) and hydrobromic acid (which is neutralised by sodium carbonate). The liquid separates into two layers—the lower insoluble layer of ethyl bromide is run out. It is washed with *water* (to remove the excess sodium carbonate). and

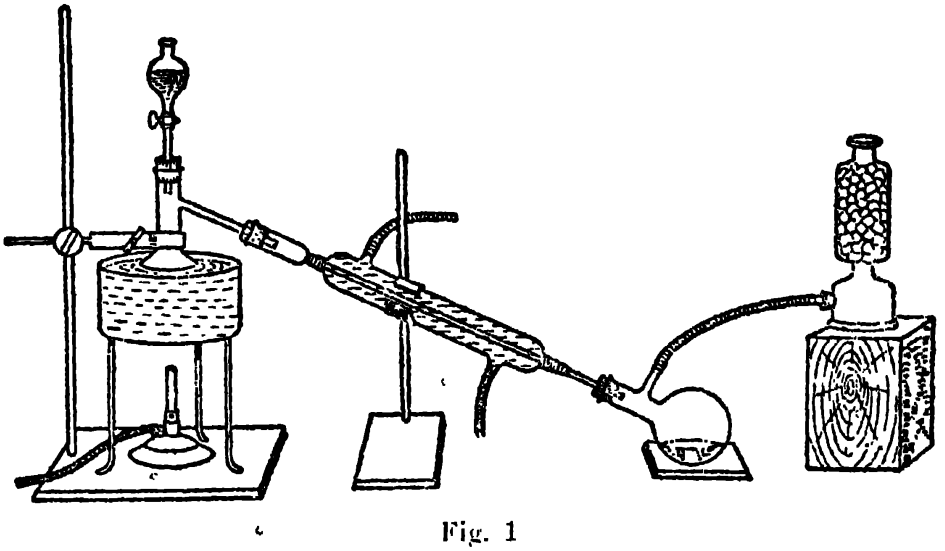


Fig. 1

then dried over anhydrous *calcium chloride* and re-distilled. The distillate between 35-40° is collected.

Ethyl iodide, C_2H_5I, is similarly made as above, using iodine in place of bromine.

Alternately, 50 c.c. of ethyl alcohol and 25 c.c. conc. H_2SO_4 are mixed together in a distilling flask, and then 50 gms of KBr are added to the *cold* mixture. The flask is fitted with a condenser and an adapter which dips in some water in a receiver (p. 49). The receiver is cooled in ice-water. The mixture is distilled from a sand bath until oily drops cease to collect in the receiver. The ethyl bromide is purified as above.

Ethyl iodide can be similarly made, using KI in place of KBr.

Methyl bromide, CH_3Br, and **methyl iodide,** CH_3I, are made by the methods used for the ethyl compounds, using methyl alcohol in place of ethyl alcohol.

Preparation of ethyl chloride.—Dry HCl gas is passed into anhydrous ethyl alcohol (containing half its weight of anhydrous zinc chloride) taken in a flask fitted with a reflux condenser. When the alcohol is saturated with the hydrogen chloride, the flask is gently warmed on a water bath—ethyl chloride (a gas, b.p. 12·5°) with some alcohol and HCl, passes off. It is bubbled through two wash-bottles containing aqueous alkali and conc. H_2SO_4 respectively, which removes HCl, alcohol and moisture. The ethyl chloride is then condensed and collected in a receiver cooled in a freezing mixture.

Methyl chloride, CH_3Cl, is similarly made, using methyl alcohol in place of ethyl alcohol.

Properties of alkyl halides.—Physical properties.—The monohalogen derivatives of paraffins are called *alkyl halides.* Most of the lower alkyl halides are colourless, pleasant-smelling liquids—some are gases. They are nearly all *heavier* than water, in which they are insoluble. They are soluble in alcohol and ether. Their boiling points in any series uniformly rise from the chloride to iodide, as the following data show:

	d. at 0°	b.p.		d. at 0°	b.p.
Methyl chloride	—	—24°	Ethyl chloride	0·921	12·5°
Methyl bromide	1·73	+4·5°	Ethyl bromide	1·47	38·5°
Methyl iodide	2·33	43°	Ethyl iodide	1·97	72·0°

Ethyl chloride is used as a local anaesthetic in dentistry, etc., and also as a refrigerant. Methyl chloride can be put to similar uses. Ethyl chloride is used for the preparation of lead tetraethyl. Methyl bromide is stored in the liquid state in aeroplanes for use as a fire extinguisher.

Chemical properties.—The alkyl halides are very reactive chemically in as much as the halogen atom can be readily replaced by other atoms or groups. Their reactivity increases from chloride via bromide, to iodide. They closely resemble each other in chemical behaviour. Their important reactions are shown below.

Synthetic uses of alkyl halides.—(i) *Reduction with nascent hydrogen gives a paraffin*: $C_2H_5I + 2H = C_2H_6$ (ethane) $+ HI$.

The nascent hydrogen is formed by the action of alcohol on zinc-copper or aluminium-mercury couple.

(ii) **Reaction with metallic sodium gives higher paraffins.**—The alkyl halide is dissolved in dry ether and sodium is added in thin slices. This is *Wurtz reaction.*

$$CH_3I + 2Na + CH_3I = CH_3-CH_3 \text{ (ethane)} + 2NaI$$

$$C_2H_5Br + 2Na + C_2H_5Br = C_2H_5 - C_2H_5 \text{ (butane)} + 2NaBr$$

(iii) (a) Magnesium combines with alkyl halide in dry ether to give magnesium alkyl halide **(Grignard reagent).** The Grignard reagent is decomposed by water, giving paraffin. This is *Grignard reaction.*

$$C_2H_5Br + Mg = C_2H_5-Mg.Br \text{ (ethyl magnesium bromide)}$$

$$C_2H_5MgBr + H.OH = C_2H_6 \text{ (ethane)} + Mg(OH)Br$$

(b) Zinc acts on alkyl halide, giving zinc alkyl which is decomposed by water, giving a paraffin.

$$2C_2H_5Br + 2Zn = Zn(C_2H_5)_2 \text{ (zinc ethyl)} + ZnBr_2$$

$$Zn(C_2H_5)_2 + 2H.OH = 2C_2H_6 + Zn(OH)_2$$

(iv) **Hydrolysis with aqueous alkali** (NaOH or KOH) or **moist silver oxide** ($AgOH$) **gives alcohols.**

$$C_2H_5I + AgOH = C_2H_5OH \text{ (ethyl alcohol)} + AgI$$

(v) **Alcoholic potash** (i.e., a solution of caustic potash, KOH in alcohol) removes a molecule of halogen acid from *neighbouring carbon atoms* of alkyl halides, giving **olefines.**

$$CH_3-CH_2I + KOH \longrightarrow CH_2=CH_2 \text{ (ethylene)} + KI + H_2O$$

Methyl iodide, CH_3I, reacts differently; it gives dimethyl ether, CH_3-O-CH_3, when similarly treated.

$$2CH_3I + 2KOH \longrightarrow CH_3 - O - CH_3 + 2KI + H_2O$$

(vi) **Ammonia forms an alkyl amine** ; the alkyl halide is heated with alcoholic ammonia in a sealed tube.

$$C_2H_5I + NH_3 + NH_3 = C_2H_5NH_2 \text{ (ethyl amine)} + NH_4I$$

(vii) **Potassium cyanide gives alkyl cyanide or nitrile ;** the alkyl halide is heated with alcoholic potassium cyanide.

$$CH_3CH_2I + KCN = CH_3CH_2CN \text{ (ethyl cyanide)} + KI$$

The alkyl cyanide on hydrolysis in presence of hot alkali or mineral acids, gives an acid.

$$CH_3CH_2CN + 2H_2O = CH_3CH_2COOH \text{ (propionic acid)} + NH_3$$

The alkyl cyanide contains *one carbon atom more than* the original alkyl halide. Hence it gives a method of **lengthening the carbon chain.**

(viii) Silver nitrite gives nitroparaffins:

$$C_2H_5Br + AgNO_2 = C_2H_5NO_2 \text{ (nitro ethane)} + AgBr$$

(ix) *Sodium alcoholate yields ethers:*

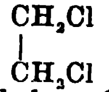
$$\underset{\text{Sodium ethoxide}}{C_2H_5ONa} + IC_2H_5 \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} + NaI$$

(x) *Silver salt of an acid gives esters:*

$$\underset{\text{Silver acetate}}{CH_3COOAg} + IC_2H_5 = \underset{\text{Ethyl acetate (an ester)}}{CH_3COOC_2H_5} + AgI$$

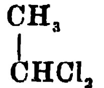
Dihalogen derivatives.—Methane forms only one dihalogen derivative of the formula CH_2X_2 (where X = Cl, Br or I). Thus, only one methylene chloride,

bromide or iodide is known. CH_2'' is known as the *methylene radical.* Ethylene, however, forms two isomeric compounds of the formula $C_2H_4X_2$ (where X = Cl, Br or I) according as the two halogen atoms are attached to the same or different carbon atoms, e.g.,



$$\begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

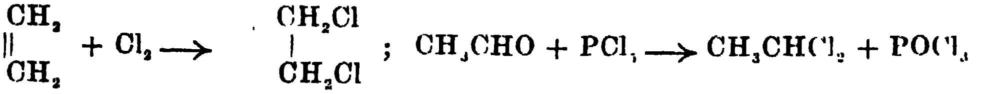
Ethylene chloride



$$\begin{array}{c} CH_3 \\ | \\ CHCl_2 \end{array}$$

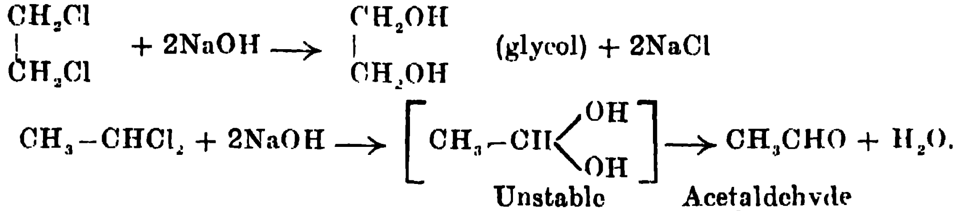
Ethylidene chloride

Ethylene and ethylidene chlorides. —Ethylene chloride or dichloroethane (b.p. 84°) is formed by the action of chlorine on ethylene. Ethylidene chloride (b.p. 58°) is formed by the action of PCl_5 on acetaldehyde, CH_3CHO.



$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + Cl_2 \longrightarrow \begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array} ; \; CH_3CHO + PCl_5 \longrightarrow CH_3CHCl_2 + POCl_3$$

On hydrolysis with aqueous alkali ethylene chloride gives glycol, CH_2OH-CH_2OH, whereas ethylidene chloride gives acetaldehyde, and hence they may be distinguished.



$$\begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array} + 2NaOH \longrightarrow \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} \text{(glycol)} + 2NaCl$$

$$CH_3-CHCl_2 + 2NaOH \longrightarrow \left[CH_3-CH\begin{array}{l} \diagup OH \\ \diagdown OH \end{array} \right] \longrightarrow CH_3CHO + H_2O.$$

Unstable Acetaldehyde

Trihalogen derivatives. —Two members of this group, e.g., chloroform and iodoform are important, because of their use in surgery and medicine.

oform, trichloromethane, $CHCl_3$, is formed when chlorine acts on methane in sunlight (p. 332). It is prepared in the laboratory and also commercially by boiling ethyl alcohol or acetone with bleaching powder and water. The bleaching powder supplies both chlorine and lime for the reaction.

(i) Alcohol is first oxidised by chlorine to acetaldehyde, CH_3CHO. The acetaldehyde reacts with more chlorine, giving trichloroacetaldehyde or chloral, $CCl_3.CHO$. The chloral is decomposed by lime into chloroform and calcium formate.

CH_3CH_2OH (ethyl alcohol) + Cl_2 = $CH_3CHO + 2HCl$

CH_3CHO (acetaldehyde) + $3Cl_2 = CCl_3CHO + 3HCl$

$Ca'OH + CCl_3.CHO$ (chloral) $= CHCl_3 + HCOOCa'$

calcium formate

(Here Ca′ stands for a half atom of calcium).

(ii) Acetone reacts with chlorine, giving trichloro acetone, which is decomposed by lime, giving chloroform and calcium acetate.

$CH_3.CO.CH_3$ (acetone) + $3Cl_2 = CCl_3.CO.CH_3 + 3HCl$

$Ca'OH + CCl_3.CO.CH_3 = CHCl_3 + CH_3COOCa'$ (calcium acetate)

(Here Ca′ stands for a half atom of calcium).

Preparation.—Fresh bleaching powder (200 gm.) is ground into a paste with water (800 c.c.) and then placed in a two-litre flask fitted with a condenser and receiver. 50 c.c. acetone, diluted with 50 c.c. water, are then added in small amounts. The flask is then heated on a water bath for about half an hour. Chloroform distils with some acetone and water, and collects as a heavy oil in the receiver. Distillation is continued until no more oily drops pass over. It is purified exactly in the same way as ethyl bromide (p. 18).

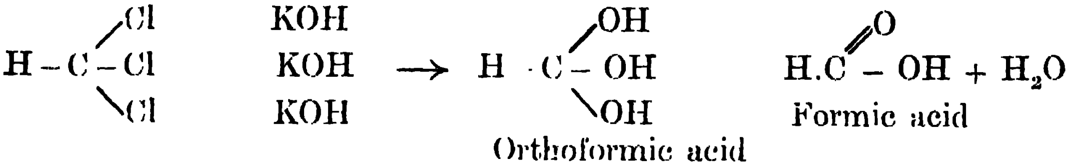
Chloroform is also made commercially by reducing carbon tetrachloride, CCl_4, with iron and water: $CCl_4 + 2H = CHCl_3 + HCl$.

Pure chloroform is made by heating chloral with aqueous caustic soda. $NaOH + CCl_3.CHO$ (chloral) $= CHCl_3 + HCOONa$

Properties.—(i) Chloroform is a heavy (sp. gr. 1·5 at 15°) colourless liquid (b.p. 61°) with a pleasant smell. It is non-inflammable. It is insoluble in water, but readily dissolves in alcohol and ether.

(ii) On hydrolysis with hot alcoholic potash, it gives potassium formate, HCOOK. $HC.Cl_3 + 4KOH = H.COOK + 3KCl + 2H_2O$

The stages in the reaction are as follows:



The intermediate compound, orthoformic acid, is unstable, and readily splits off water, forming formic acid.

(iii) When chloroform is warmed with few drops of aniline, $C_6H_5NH_2$, **and alcoholic potash,** an extremely nauseating smell is produced, owing to the formation of highly poisonous *phenyl carbylamine* or *phenyl isocyanide*, C_6H_5NC. This forms a delicate *test* for chloroform and is known as the **carbylamine reaction.**

$$C_6H_5NH_2 + CHCl_3 + 3KOH = C_6H_5NC + 3KCl + 3H_2O$$

Uses.—Chloroform is used, usually mixed with ether, in surgery as an anæsthetic—its vapour produces unconsciousness on inhalation. But chloroform for anæsthetic purpose must be strictly pure.

In presence of sunlight and air, chloroform slowly decomposes into HCl and carbonyl chloride (or phosgene), $COCl_2$, which is highly poisonous.

$$2CHCl_3 + O_2 = 2COCl_2 + 2HCl$$

The presence of products of decomposition may be ascertained by adding silver nitrate solution which forms a white precipitate of silver chloride, if COCl, or HCl is present. Pure chloroform gives no precipitate with silver nitrate solution. Chloroform for anæsthetic purposes should be kept in well-stoppered bottles of dark blue or brown glass, full to the neck, with addition of about one per cent alcohol (which arrests the decomposition of chloroform). Even then it is derisable to keep the bottles in the dark. Chloroform is an excellent solvent for many oragnic substances; it dissolves fats, oils, rubber, etc. Chloroform combines with acetone, to give *chloretone*, which is a hypnotic.

Iodoform, CHI_3, is an important antiseptic. It is used in antiseptic surgery as a dressing for wounds. Iodoform is a lemon-yellow crystalline solid (m.p. 119°) with a strong unpleasant smell. It readily sublimes and hence can be purified by sublimation. It is insoluble in water, but dissolves in hot alcohol. It is decomposed by boiling caustic soda (or potash), giving sodium (or potassium) formate:

$$CHI_3 + 4NaOH = HCOONa + 3NaI + 2H_2O$$

Preparation.—Iodoform is made from ethyl alcohol or acetone by the action of sodium hypoiodite, NaOI, and caustic soda (or iodine and caustic soda). But since hypoiodite is unstable, a mixture of NaI and sodium hypochlorite, NaOCl, is generally used, which react to form NaOI *in situ*. The steps in the reaction are as follows:

$$NaOCl + NaI = NaOI + NaCl$$

$$CH_3-CO-CH_3 + 3NaOI = CH_3-CO-CI_3 + 3NaOH$$

Acetone is iodinated by NaOI to form triodoacetone, $CH_3-CO-CI_3$, which is decomposed by alkali, giving ioodform and sodium acetate.

$$CH_3.CO.CI_3 + HONa = CHI_3 + CH_3COONa$$

Alcohol is oxidised to acetaldehyde, CH_3CHO, which then reacts with NaOI, giving iodal, $CI_3.CHO$. The iodal is decomposed by alkali, giving iodoform and sodium formate.

$$CH_3.CH_2OH + NaOI = CH_3CHO + NaI + H_2O$$

$$CH_3.CHO + 3NaOI = CI_3.CHO + 3NaOH$$

$$NaOH + CI_3.CHO = CHI_3 + HCOONa$$

Preparation of iodoform.—20 gms. of sodium carbonate are dissolved in 50 c.c. of water, 10 c.c. of ethyl alcohol are poured into the solution, and 12 gms. of iodine added in small portions. The liquid is kept at 60-80°. *The iodoform may get hydrolysed if the temperature exceeds 80°.* When the colour of iodine has almost disappeared, the liquid is cooled when iodoform crystallises out in hexagonal plates.

Acetone is prepared commercially by electrolysis of an aqueous solution of potassium iodide and sodium carbonate in prsence of alcohol or acetone at 60-65°. Iodoform is obtained at the anode. The iodine liberated at the anode, forms *hypoiodite* which then acts on alcohol (or acetone), giving iodoform.

Haloform reaction.—When acetone (or ethyl alcohol) is heated with an aqueous solution of hypohalite (NaOCl, NaOBr, or NaOI) and caustic soda, chloroform, bromoform, $CHBr_3$ or iodoform, is formed. The reaction depends on the combined oxidising and halogenating action of the hypohalite, as illustrated above in the case of iodoform. This is known as *haloform reaction*. Bromoform, $CHBr_3$, is a colourless liquid.

Carbon tetrachloride, CCl_4, is made by passing chlorine into carbon disulphide in presence of metallic iron or iodine as catalyst.

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2 \text{ (sulphur monochloride)}$$

It is a colourless, non-inflammable liquid (b.p. 76·5°) with a sweet smell like chloroform. It is heavier than water (sp. gr. 1·60 at 15°) and also insoluble in it. It is used as a solvent for extraction of fats and oils. It is a solvent for wax and grease. Because of its non-inflammability, it is used in dry cleaning of clothes, and also as a fire extinguisher (trade name, pyrene) particularly in fires in chemical laboratories or in oil fires—the heavy carbon tetrachloride vapour hangs as a cloud over the fire and extinguishes it.

Dichlorodifluoro methane, CCl_2F_2, is made from carbon tetrachloride and antimony trifluoride.

$$3CCl_4 + 2SbF_3 = 3CCl_2F_2 + 2SbCl_3$$

It is a gas which boils at −30°. It is used as a refrigerant under the name *freon*, as it is non-toxic, non-inflammable and does not corrode metals.

V

ALCOHOLS

Alcohols.—The alcohols may be looked as paraffins in which one or more hydrogen atoms are replaced by hyrdoxyl groups, OH. The alcohols are, therefore, hydroxyl derivatives of paraffins. According to the number of OH groups present in the compound, they are called *mono-*, *di-*, *tri-*, etc., *hydric* alcohols. Alcohols containing more than one OH group, are in general, known as polyhydric alcohols.

Paraffin	*Name of alcohol*	*Class*
Methane, CH_4	Methyl alcohol, CH_3OH	Monohydric alcohol
Ethane, C_2H_6	Ethyl alcohol, CH_3CH_2OH	,, ,,
	Glycol, $CH_2OH.CH_2OH$	Dihydric
Propane, C_3H_8	Glycerol, $CH_2OH.CHOH.CH_2OH$	Trihydric

Monohydric alcohols.—They are mono-hydroxy derivatives of paraffins. They contain an alkyl group attached to a hydroxyl and have the general formula $C_nH_{2n+1}OH$.

They are named from the corresponding paraffin by replacing the suffix -'*ane*' by -'*yl*' (or by deleting final '*e*' and adding the ending '*ol*').

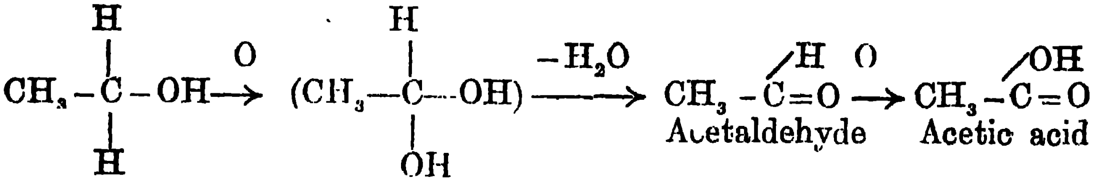
Methane, CH_4	Methyl alcohol, methanol, CH_3OH
Ethane, C_2H_6	Ethyl alcohol, ethanol, C_2H_5OH
Propane, C_3H_8	Propyl alcohol, propanol, C_3H_7OH

An alcohol is known as **primary, secondary,** or **tertiary,** according as it contains a $-CH_2OH$, $=CHOH$, or a $\vert\!\vert\!\vert C.OH$ group in the molecule.

Type of alcohol	*Typical group*	*Example*
Primary alcohol	$-CH_2OH$	Methyl alcohol, $H.CH_2OH$ Ethyl alcohol, $CH_3.CH_2OH$ Normal propyl alcohol $CH_3.CH_2.CH_2OH$
Secondary alcohol	$>CHOH$	Isopropyl alcohol or secondary propyl alcohol, $CH_3-CHOH-CH_3$
Tertiary alcohol	$\overset{\diagdown}{\underset{\diagup}{-}}C.OH$	Tertiary butyl alcohol, $CH_3-\underset{\underset{CH_3}{\vert}}{C(OH)}-CH_3$

In one system of naming, methyl alcohol is given the name *carbinol*; other alcohols are considered as alkyl derivatives of carbinol. Thus, ethyl alcohol is methyl carbinol, n-propyl alcohol is ethyl carbinol, *sec-propyl* alcohol, dimethyl carbinol, tertiary butyl alcohol, trimethyl carbinol, and so on.

A **primary alcohol** on oxidation first gives an *aldehyde*, and then *acid* containing the *same* number of carbon atoms as the alcohol.

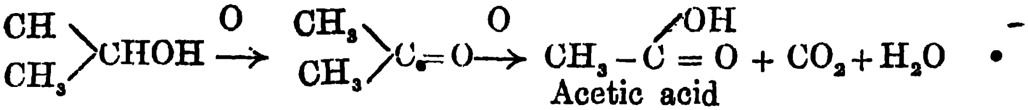


$$CH_3-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-OH \xrightarrow{O} (CH_3-\underset{\underset{OH}{\vert}}{\overset{\overset{H}{\vert}}{C}}-OH) \xrightarrow{-H_2O} CH_3-\overset{\diagup H}{C}=O \xrightarrow{O} CH_3-\overset{\diagup OH}{C}=O$$

Ethyl alcohol Not isolated Acetaldehyde Acetic acid

A compound contaning two or more OH groups attached to the same carbon atom, is usually unstable and readily splits off water.

A secondary alcohol on oxidation gives a *ketone* with the *same* numbers of carbon atoms as the alcohol, and then acids with *fewer* carbon atoms, on further oxidation.

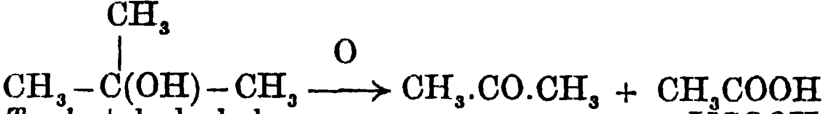


$$\begin{matrix}CH\\CH_3\end{matrix}\!\!>CHOH \xrightarrow{O} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O \xrightarrow{O} CH_3-\overset{OH}{C}=O + CO_2 + H_2O$$

Acetic acid

Sec—propyl alcohol Acetone

A tertiary alcohol on drastic oxidation gives a mixture of ketones and acids, each with *fewer* carbon atoms than the alcohol.



$$CH_3-\overset{CH_3}{\overset{|}{C}}(OH)-CH_3 \xrightarrow{O} CH_3.CO.CH_3 + CH_3COOH + HCOOH + CO_2 + H_2O, \text{ etc.}$$

Ter-butyl alcohol

The three types of alcohols may be *distinguished* in this way.

Methyl alcohol, methanol, carbinol, CH_3OH, occurs in combination in many plants, e.g., oil of wintergrun (methyl salicylate).

It is made by two methods: (i) **by distillation of wood.**—One of the products of dry distillation of wood is the aqueous distillate *pyroligneous acid* (p. 319), which consists mainly of about 1% methyl alcohols, 5-8% acetic acid and 0.1% acetone. The pyroligneous acid is first neutralised with milk of lime, whereby acetic acid is converted into calcium acetate and then distilled—the methyl alcohol together with acetone and some water passes into the distillate and calcium acetate is left behind as a residue. The methyl alcohol (b.p. 65°) is then separated from most of the acetone (b.p. 56°) by careful fractional distillation. The methyl alcohol may be *dried* by standing over quick lime, followed by redistillation. The last trace of water may be removed by distillation over metallic calcium. But the methyl alcohol thus prepared invariably contains about 1—2 per cent acetone.

The methyl alcohol may be made *acetone-free* by treatment with anhydrous calcium chloride, when the solid compound, $CaCl_2.4CH_3OH$, crystallises out. The calcium chloride compound on heating gives pure methyl alcohol which is condensed and collected.

Methyl alcohol is also called **wood spirit** or **wood naphtha,** as it is made by distillation of wood.

(ii) **by synthetic process.**—Synthetic methyl alcohol is produced by passing a mixture of purified water gas (a mixture of CO and H_2 in nearly equal volumes, made by passing steam over heated coke) with half its volume of hydrogen under a pressure of 200 atmospheres over a catalyst of zinc and chromium oxides, heated to about 400°. The synthetic methyl alcohol is acetone-free.

$$(CO + H_2) + H_2 = CH_3OH$$

Properties.—Methyl alcohol is a colourless liquid (b.p. 64·7°) with a wine-like smell and a burning taste. It is miscible with water (sp. gr. 0·796 at 15°) and ether. It is inflammable and burns with a pale blue non-luminous flame. It is definitely poisonous, causing blindness and madness, and hence its use to *denature* ethyl alcohol (i.e., to make it unfit to drink) in making *methylated spirit.* Methyl alcohol closely resembles ethyl alcohol in chemical properties but it differs in its action upon human body.

ctions. —(i) Metallic sodium rapidly attacks methyl alcohol, giving sodium *methoxide* (a white deliquescent solid) and evolving H_2.

$$2CH_3OH + 2Na = 2CH_3ONa \text{ (sodium methoxide)} + H_2$$

Sodium methoxide is decomposed by water, giving back the methyl alcohol. Potassium methoxide, CH_3OK, reacts similarly.

$$CH_3ONa + H.OH = CH_3OH + NaOH$$

(ii) PCl_5 acts on methyl alcohol, giving methyl chloride, $POCl_3$ and hydrogen chloride. $CH_3OH + PCl_5 = CH_3Cl + POCl_3 + HCl$

(iii) reacts with acids in presence of dehydrating agents, e.g., conc. H_2 HCl gas, etc., to give *ester* and water.

(a) With HCl gas in presence of anhydrous $ZnCl_2$, it gives methyl chloride. HBr and HI react similarly.

$$CH_3OH + HCl \rightleftharpoons CH_3Cl + H_2O$$

(b) With acetic acid in presence of conc. H_2SO_4 it yields methyl acetate, CH_3COOH_3, and water

$$CH_3COOH + HOCH_3 \rightleftharpoons CH_3COOCH_3 + H_2O$$

(c) With concentrated sulphuric acid, it forms methyl hydrogen sulphate and water:

$$CH_3OH + H_2SO_4 \rightleftharpoons CH_3HSO_4 + H_2O$$

(iv) With red phosphorus and bromine (or iodine) it gives methyl bromide (or iodide): $PBr_3 + 3CH_3OH = 3CH_3Br + H_3PO_3$.

(v) Methyl alcohol is a primary alcohol ; on oxidation it first gives formaldehyde, then formic acid, and finally CO_2 and water:

$$H.CH_2OH + O = H.CHO \text{ (formaldehyde)} + H_2O$$

$$H.CHO + O = H.COOH \text{ (formic acid)}$$

$$H.COOH + O = CO_2 + H_2O$$

Formaldehyde is prepared by passing a mixture of methyl alcohol vapour and air over copper or silver gauze, heated to about 400°.

Uses of methy alcohol. —Methyl alcohol is used : (i) in making methylated spirit, and in the preparation of formaldehyde, various dye intermediates and perfumes, (ii) as a solvent for shellacs and resins in the preparation of varnishes, (iii) as an anti-freeze in radiators of motor cars, and (iv) as a motor fuel mixed with petrol.

Ethyl alcohol, ethanol, C_2H_5OH, is simply called 'alcohol', also known as *grain alcohol* or *spirit of wine* in commerce. It is usually made by *fermentation* of certain sugars, such as glucose and cane sugar, by yeast. Thus, when yeast is added to a solution of glucose at the room temperature, the liquid shortly begins to forth, giving the appearance of boiling. The process is known as *fermentation* from the Latin *fervere*, to boil. The glucose is decomposed into ethyl alcohol and carbon dioxide during fermentation:

$$C_6H_{12}O_6 \text{(glucose)} = 2C_2H_5OH + 2CO_2$$

The decomposition is effected by certain substance, called **enzymes,** which are produced by yeast during its growth.

The enzymes are complex organic substances which act as catalysts. Yeast is a low form of plant life consisting of one cell only.

Fermentation is, therefore, a process of decomposition of complex organic substances into simpler ones, brought about by enzymes (produced by yeast, etc.) which act as catalysts in the process. The *ferment* or the *enzyme*, called *zymase*, present in yeast cells, converts glucose into alcohol and carbon dioxide. The change of glucose (or fructose) into ethyl alcohol is known as **alcoholic fermentation.**

Although a living organism yeast is used in the alcoholic fermentation, the process is *merely a chemical reaction*, since the zymase extractod by a process in which the yeast cells are destroyed, sets in fermentation like the living yeast.

The yeast contains several enzymes ; among which are *zymase*, *invertase* and *maltase*. Invertase catalyses the decomposition of cane sugar by hydrolysis into glucose, $C_6H_{12}O_6$, and fructose, $C_6H_{12}O_6$.

$C_{12}H_{22}O_{11}$ (cane sugar) $+ H_2O = C_6H_{12}O_6 + C_6H_{12}C_6$

Maltase converts maltose (a sugar isomeric with cane sugar) into two molecules of glucose.

$C_{12}H_{22}O_{11}$ (maltose) $+ H_2O = 2C_6H_{12}O_6$ (glucose)

Invertase and maltase are thus hydrolytic enzymes. Zymase, as already stated, brings about alcoholic fermentation.

Manufacture.—Ethyl alcohol is made from cheap raw materials: (i) molasses, (ii) starchy materials such as rice, maize, potato, etc.

(i) Molasses is the mother liquor left after crystallisation of cane-sugar from the concentrated cane juice. It contains about 50-60 per cent cane sugar. It is available from sugar mills and is an important source of alcohol in India and elsewhere.

The molasses is diluted with water to about 10-15 per cent sugar, and is fermented by adding yeast in slightly acid medium. The yeast has a double function upon the cane sugar—the enzyme *invertase* converts it into glucose and fructose, which are then fermented into ethyl alcohol under the influence of *zymase*, as already stated. The fermented liquor contains 6—12% alcohol. The process takes about 2 days.

(iii) The starch-containing materials, such as rice and potato, are reduced to a pulp or a paste with water, and then mixed with a little *malt*. Starch is not directly fermentable by yeast, and must, therefore, be first converted into sugar. The enzyme *diastase* present in germinating barley ('malt') converts starch into the sugar, *maltose*, $C_{12}H_{22}O_{11}$. The mixture is kept at about 50° for about 30-60 minutes, when maltose is formed. $2(C_6H_{10}O_5)_n$ (starch) $+ nH_2O = nC_{12}H_{22}O_{11}$ (maltose).

The liquid is then cooled to about 25° and mixed with yeast. The mixture is kept for 2-3 days, when the maltose is first converted into glucose, which then undergoes alcoholic fermentation, in a manner as stated above.

The weak solution of alcohol (6-12%) is then submitted to fractional distillation in large stills (e.g., Coffey's still) using a fractionating column, whereby a distillate containing about 95·6% alcohol is obtained and is commercially known as **rectified spirit.** But absolute alcohol, free from water, cannot be made by the above method as a constant boiling mixture of 95·6% alcohol and 4·4% water, boiling at 78·15°, distils over. The **absolute alcohol** is made in two ways:

(i) The rectified spirit is dried by standing over quick lime, and then distilled. But it still contains traces of water which may be removed by adding calculated amount of Na or Ca, and then re-distilling.

(ii) The rectified spirit is mixed with a little benzene and distilled. Distillation yields first (a) a mixture of benzene, alcohol and water (b.p. 64·8), then (b) a mixture of benzene and alcohol, (b.p. 68·2) and finally (c) a distillate of pure anhydrous alcohol (b.p. 78·5).

The anhydrous alcohol is known as *absolute alcohol.*

Synthetic ethyl alcohol is made from ethylene (which is obtained from cracked petroleum). Ethylene is absorbed in concentrated sulphuric acid, and the resulting ethyl hydrogen sulphate. $C_2H_5HSO_4$, when heated with dilute sulphuric acid, undergoes hydrolysis, giving ethyl alcohol.

$$CH_2 = CH_2 + H_2SO_4 = CH_3-CH_2.HSO_4$$
$$CH_3-CH_2.HSO_4 + H.OH = CH_3\text{-}CH_2OH + H_2SO_4$$

Properties. —Pure ethyl alcohol is a colourless liquid (b.p. 78·5° ; sp. gr. 0·790 at 15°) with a pleasant vinous smell and a burning taste. It is inflammable and burns with a pale blue flame. It is miscible with water with evolution of heat and contraction in volume. The alcohol itself is very hygroscopic. It is also miscible with ether. It freezes at—114° and hence its use in alcohol thermometers. Bromine, iodine, sulphur, and phosphorus, all dissolve in ethyl alcohol. In small doses the alcohol is a good stimulant, but in larger doses causes blurring of senses and finally unconsciousness.

Quick lime is a suitable drying agent for alcohol. Calcium chloride *cannot* be used, as it combines with the alcohol, yielding a compound, $CaCl_24C_2H_5OH$, containing alcohol of crystallisation.

Reactions. —The important reactions of ethyl alcohol (a typical monohydric alcohol) are :

(i) Metallic sodium (or potassium) vigorously reacts with alcohol, evolving hydrogen and forming *ethoxide* or *ethylate* (white crystalline deliquescent solid).

$$2C_2H_5OH + 2Na = 2C_2H_5ONa \text{ (sodium ethoxide) } + H_2$$

Metallic Ca, Mg, etc., also react similarly but less rapidly. The reaction is used to remove traces of water from alcohol.

The ethoxides are readily hydrolysed by water, giving back alcohol.

$$C_2H_5ONa + H.OH = C_2H_5OH + NaOH$$

(ii) PCl_5 reacts, forming ethyl chloride, $POCl_3$ and HCl.

$$C_2H_5OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl$$

Reactions (i) and (ii) detect OH group in alcohols.

(iii) It reacts with acids in presence of a dehydrating agent, such as concentrated H_2SO_4, HCl gas, etc., forming an *ester* and water.

$$\text{Alcohol + acid} \rightleftharpoons \text{ester + water.}$$

The process of esterification is reversible. The dehydrating agent absorbs the water formed, and thereby the reaction may be made complete.

(a) Acetic acid acts on ethyl alcohol in presence of conc.

H_2SO_4, giving the ester, ethyl acetate, $CH_3COOC_2H_5$, which has a fruity smell.

$$CH_3COOH + HOC_2H_5 \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(b) HCl gas reacts in presence of anhydrous zinc chloride, giving ethyl chloride. HBr and HI act similarly.

$$C_2H_5OH + HCl \rightleftharpoons C_2H_5Cl + H_2O$$

(c) Concentrated H_2SO_4 reacts with ethyl alcohol, giving ethyl hydrogen sulphate. $C_2H_5OH + H_2SO_4 \rightleftharpoons C_2H_5HSO_4 + H_2O$

The ethyl hydrogen sulphate, on hydrolysis with hot dilute H_2SO_4, gives back the alcohol.

2 At about 140° ethyl hydrogen sulphate reacts with more alcohol, giving diethyl ether, $C_2H_5-O-C_2H_5$.

$$C_2H_5HSO_4 + HOC_2H_5 = C_2H_5-O-C_2H_5 + H_2SO_4$$

At a still higher temperature, about 180°, ethyl hydrogen sulphate gives ethylene. $C_2H_5HSO_4 \rightleftharpoons CH_2=CH_2 + H_2SO_4$

(iv) Oxidising agents, e.g., $K_2Cr_2O_7$ and conc. H_2SO_4, convert the alcohol first into acetaldehyde, CH_3CHO, and finally into acetic acid.

$$CH_3CH_2OH + O = CH_3CHO + H_2O; \quad CH_3CHO + O = CH_3COOH$$

Dehydrogenation by passing the alcohol vapour over heated copper at 300°, also forms acetaldehyde. $CH_3CH_2OH = CH_3CHO + H_2$.

(v) Dehydration of alcohol by passing over alumina at 350° gives ethylene. Concentrated H_2SO_4 also dehydrates ethyl alcohol:

$$C_2H_5OH \rightarrow CH_2 = CH_2 + H_2O.$$

(vi) Red P and bromine (or iodine) act on alcohol, giving ethyl bromide (or iodide) (p. 18). $PBr_3 + 3C_2H_5OH = 3C_2H_5Br + H_3PO_3$

(vii) Chlorine acts on ethyl alcohol, first giving acetaldehyde, and finally trichloro-acetaldehyde or chloral, CCl_3CHO (p. 21). Bromine reacts similarly, giving bromal, $CBr_3.CHO$, but iodine has no action.

$$CH_3CH_2OH + Cl_2 = CH_3CHO + 2HCl$$

$$CH_3CHO + 3Cl_2 = CCl_3.CHO + 3HCl$$

(viii) Action of bleaching powder and water gives chloroform.

(ix) Iodine reacts in presence of aqueous alkali, giving iodoform.

Presence of traces of water in alcohol may be detected by adding anhydrous copper sulphate which turns blue, or by adding few drops of benzene or petroleum ether which gets turbid, if any water is present:

Distinctive tests for methyl and ethyl alcohols. —Use aqueous solutions of methyl and ethyl alcohols.

Reagent	Methyl alcohol	Ethyl alcohol
(i) Iodine + NaOH warm*	No iodoform	Yellow crystals of iodoform
(ii) $K_2Cr_2O_7 + H_2SO_4$ (1:1) Distil	Distillate is formic acid	Distillate is acetaldehyde
(iii) Acetic acid + concentrated H_2SO_4. Warm	No characteristic smell	Fruity smell of ethyl acetate
(iv) Salicylic acid + concentrated H_2SO_4. Warm	Smell of oil of winter green	No characteristic smell
(v) Plunge red-hot Cu-gauge into the solution**	Formaldehyde is formed	Acetaldehyde is formed

* A few crystals of iodine (or a solution of iodine in potassium iodide) is added to the aqueous solution of alcohol. The mixture is warmed and caustic soda solution is added, drop or drop, until the colour of iodine disappears. Yellow crystals of iodoform with characteristic smell are deposited on cooling. Methyl alcohol does not give iodoform test. But acetone which is a common impurity in methyl alcohol responds to this test. Therefore, a negative iodoform test with a sample of methyl alcohol shows absence of acetone in it.

** Both formaldehyde and acetaldehyde give a violet colour with Schiff's reagent at ordinary temperature.

Uses of ethyl alcohol.—The uses of alcohol is very extensive. It is used : (i) in making iodoform, chlorofrm, ether, acetaldehyde, vinegar, and transparent soaps, (ii) in the preparation of dyes, drugs, perfumes (ethyl esters make fruit essences and perfumes), synthetic rubber, and rayon, (iii) in the preparations of **tinctures** (alcoholic solutions or extracts of medicinal substances), e.g., tincture of iodine, and tonics, (iv) as alcoholic beverages, e.g., wine, beer, etc., (v) as a solvent for gums and resins in making lacquers and varnishes, (vi) as a preservative of biological specimens and for sterilisation in surgergy, (vii) as an anti-freeze in radiators, (ix) as a fuel in internal combustion engines. Mixed with petrol, it is used in automobiles. The alcohol thus used in getting power is often called *power alcohol*, and (x) in making methylated spirit.

Methylated spirit.—All the alcoholic beverages are subject to high excise duty. But 'denatured' alcohol, unfit for drinking purposes but suitable for general scientific and industrial work, is duty-free, and therefore, cheap. The denatured alcohol is known as methylated spirit, and consists of about 90% rectified spirit, 10% wood spirit and a little pyridine. The methyl alcohol (wood spirit) and pyridine render the alcohol poisonous and unpalatable and consequently unfit to drink. The methylated spirit is used in making dyestuffs, varnishes and fine chemicals. It is used in spirit lamps.

Solidified spirit is made by dissolving soap in rectified spirit, and then cooling the solution, when it sets to a solid mass. It is easily ignited and is used in lamps. Approximate percentage of alcohol in several alcoholic beverages are :

Beer 2-5; wine 7-11; claret 7; sherry 16; port 20; whisky, brandy, rum 35-40.

The percentage of alcohol in pharmaceutical preparations is high : tincture of iodine 80-85; spirit of ammonia 62-68; spirit of camphor 80-87.

The percentage of alcohol in a sample of aqueous spirit, e.g., rectified spirit, is readily determined by measuring the specific gravity with a hydrometer and then referring to standard tables in which sp. gr. of any mixture of alcohol and water is given.*

VI

ETHERS

The ethers.—The ethers have the structural formulae $R—O—R'$, where R and R′ may be identical or different alkyl groups. If the two alkyl groups are identical, we get a *simple ether*, e.g.,

CH_3-O-CH_3 Dimethyl ether

C_2H_5-O-C_2H_5 Diethyl ether

But if the two alkyl groups are different, we get a *mixed ether*, e.g.,

CH_3-O-C_2H_5 Methyl ethyl ether

C_2H_5-O-C_3H_7 Ethyl propyl ether

Ethers may also be looked upon as alcohols in which the H of the ROH is replaced by an alkyl group by reaction between two molecules of alcohol with elimination of water. $ROH + HOR - R\text{-}O\text{-}R + H_2O$.

The ethers have the general formula $C_n H_{2n+2}O$, and that for alcohols is $C_nH_{2n+1}.OH$. Ethers, are therefore, isomeric with alcohols, but they differ widely in properties.

The ethers are colourless, neutral substances like the alcohols. But an ether is *much more volatile* than the isomeric alcohol. Thus, dimethyl ether, CH_3-O-CH_3, which is isomeric with ethyl alcohol, C_2H_5OH, (b.p. 78·5°) is a gas (b.p. −23·6°). Diethyl ether, $C_2H_5.O.C_2H_5$, which has the same molecular formula as butyl alcohol, $C_4H_9.OH$, boils at 34°. Normal primary butyl alcohol, $CH_3.CH_2.CH_2.CH_2OH$, boils at 117°. The ethers are *lighter than water* in which they are very much *less soluble* than the alcohols. The ethers do not react with metallic sodium or phosphorus pentachloride in the cold, and hence they do not contain any hydroxyl group like the alcohols. The low boiling ethers are *highly inflammable*.

Diethyl ether, C_2H_5-O-C_2H_5, is commonly called ether. (i) It is made in the laboratory and also in industry by distilling an excess of ethyl alcohol with strong sulphuric acid at 130-140°. At first alcohol reacts with sulphuric acid, forming ethyl hydrogen sulphate. This then reacts with more alcohol, giving ether and regenerating the sulphuric acid. $C_2H_5OH + H_2SO_4 \rightleftharpoons C_2H_5HSO_4 + H_2O$

$$C_2H_5HSO_4 + HOC_2H_5 = C_2H_5\text{-}O\text{-}C_2H_5 + H_2SO_4$$

Theoretically no sulphuric acid is used up ; the generated acid goes through the process over again, and hence the name *continuous etherification process*.

But in actual practice some sulphuric acid is reduced by side reactions, and also the acid eventually gets diluted with the water, when formation of ether ceases.

Preparation. —Equal volumes (100 c.c. each) of absolute ethyl alcohol and concentrated sulphuric acid are taken in a distilling flask fitted with a tap funnel and a thermometer (which dips in the liquid), and connected to a condenser and receiver. Ice-cold water circulates through the condenser and the receiver is cooled in ice. The flask is heated on a sand bath and kept at about 140°, when ether begins to pass over. Fresh alcohol (150 c.c.) is run in from the tap funnel at the same rate as the ether distils and collects in the receiver.

To avoid fire hazard (ether being highly inflammable), the side tube of the receiver is connected by a rubber tubing to the sink.

The distillate (which contains ether, alcohol, water, SO_2, etc.) is shaken with dilute aqueous alkali in a separating funnel, and then the lower aqueous layer is drawn off. The ether is then dried over anhydrous calcium chloride and distilled from a water-bath. The distillate is finally dried over metallic sodium (to remove traces of moisture) and re-distilled.

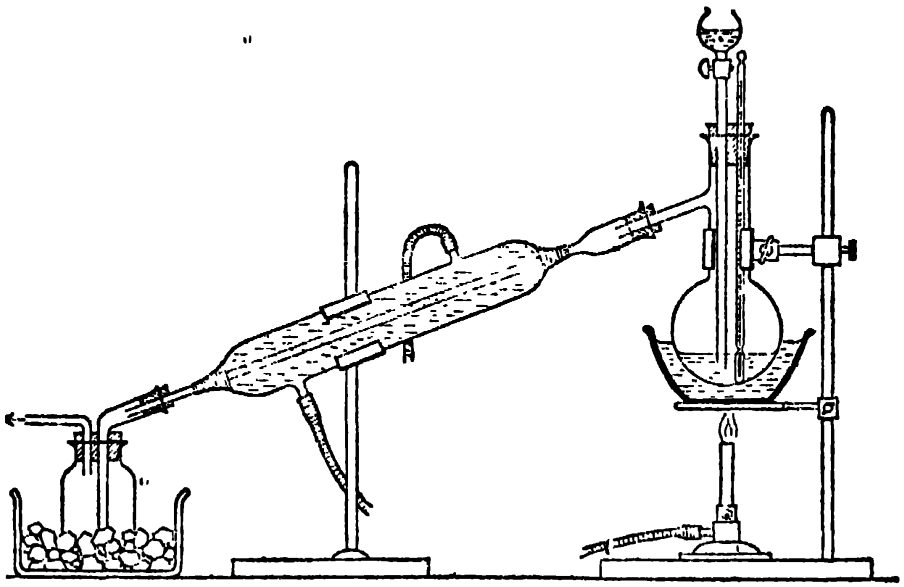


Fig. 2

Dimethyl ether $CH_3.O.CH_3$, is similarly prepared, using methyl alcohol in place of ethyl alcohol.

By mixing one alcohol, e.g., C_2H_5OH, with the sulphuric acid and running in another alcohol, e.g., CH_3OH, from the tap funnel, mixed ether may be prepared : $C_2H_5HSO_4 + HOCH_3 = C_2H_5\text{-}O\text{-}CH_3 + H_2SO_4$.

(ii) Ether is formed by heating sodium ethoxide with ethyl iodide **(Williamson's synthesis).** $C_2H_5ONa + IC_2H_5 = C_2H_5\text{-}O\text{-}C_2H_5 + NaI$

The reaction shows the structure of ether. Heating methyl iodide with sodium methoxide gives dimethy ether.

$$CH_3ONa + ICH_3 = CH_3\text{-}O\text{-}CH_3 + NaI$$

A mixed ether is formed by heating alkyl iodide with sodium alcoholate containing different alkyl radicals.

$$CH_3ONa + IC_2H_5 = CH_3\text{-}O\text{-}C_2H_5 + NaI$$

Properties of ethyl ether. —Ether is a colourless, pleasant-smelling, neutral liquid. It is very volatile (b.p. 34·6° ; m.p. —117·6°) and highly inflammable, and its vapour form an explosive mixture with air. It is lighter than water (sp. gr. 0·713 at 20°), and is slightly soluble in water, but is miscible with alcohol in all proportions. Ether possesses anaesthetic action, and causes unconsciousness on inhalations. When employed in the form of spray, it causes local insensibility by quick evaporation and cooling, and hence its use as a local anaesthetic.

Reactions. —Compared with alcohol ether is somewhat inert chemically. (i) Ether does not react with sodium or potassium, nor does it react with PCl_5 in the cold, showing the absence of OH group in ether (cf. alcohols). Ether, however, reacts with PCl_5 on heating, giving ethyl chloride: $(C_2H_5)_2O+PCl_5 = 2C_2H_5Cl+POCl_3$

(ii) Strong hydriodic acid decomposes ether on heating, giving ethyl iodide. $C_2H_5\text{-}O\text{-}C_2H_5+2HI = 2C_2H_5I+H_2O$

In general, heating with HI decomposes an ether, giving alkyl iodides. By identifying the alkyl iodides, the composition of ether, (simple or mixed ether) may be determined. Thus, ethyl ether gives only ethyl iodide, but methyl ethyl ether gives CH_3I and C_2H_5I. The alkyl iodides are separated by distillation and identified by their boiling points. $CH_3\text{-}O\text{-}C_2H_5+2HI = CH_3I+H_2O+C_2H_5I$

(iii) Concentrated sulphuric acid decomposes ether.

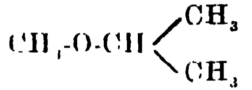
$$C_2H_5OC_2H_5+2H_2SO_4 = 2C_2H_5HSO_4 + H_2O$$

Ether is hydrolysed on heating with dilute sulphuric acid under pressure. $C_2H_5\text{-}O\text{-}C_2H_5+H_2O = 2C_2H_5OH$

All experiments with ether require careful handling to avoid fire hazard.

Uses.—Ether is largely used as a solvent for fats, oils, resins and alkaloids. It is often used in the laboratory for extraction of substances from aqueous solutions or suspensions. Mixed with alcohol, it is used as a petrol substitute. In a mixture with nitrous oxide and oxygen, it is used as an anæsthetic in surgery; a mixture of alcohol, chloroform and ether (A.C.E.) is also used as an anæsthetic.

Metamerism.—The formula $C_4H_{10}O$ stands for three isomeric ethers.



$CH_3\text{-}O\text{-}CH(CH_3)_2$

Methyl isopropyl ether

$CH_3\text{-}O\text{-}C_3H_7$

Methyl propyl ether

$C_2H_5\text{-}O\text{-}C_2H_5$

Diethyl ether

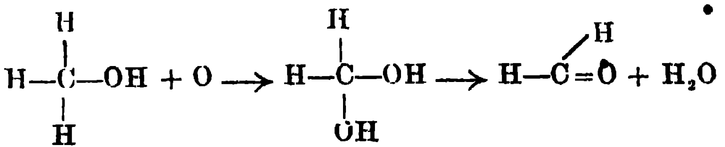
Isomers such as these, which are compounds of the same series and differ only in the composition of alkyl radicals attached to the oxygen atom are known as *metamers*, and this type of isomerism is known as *metamerism*.

The composition of the particular ether may be determined by heating with HI and identifying the alkyl iodides formed.

VII

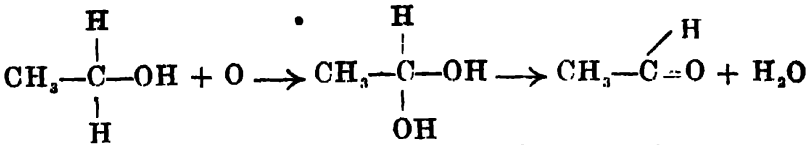
ALDEHYDES AND KETONES

Aldehydes and ketones.—A primary alcohol on mild oxidation yields ~~an *aldehyde*~~, ~~which~~ contain two hydrogen atoms less than the alcohol and hence the aldehyde from *alcohol dehyd*rogenation (alcohol dehydrogenation). On cautious oxidation methyl alcohol gives formaldehyde, and ethyl alcohol acetaldehyde:



$$H\text{—}\overset{H}{\underset{H}{C}}\text{—}OH + O \longrightarrow H\text{—}\overset{H}{\underset{OH}{C}}\text{—}OH \longrightarrow H\text{—}\overset{H}{C}{=}O + H_2O$$

Methyl alcohol Unstable intermediate Formaldehyde



$$CH_3\text{—}\overset{H}{\underset{H}{C}}\text{—}OH + O \longrightarrow CH_3\text{—}\overset{H}{\underset{OH}{C}}\text{—}OH \longrightarrow CH_3\text{—}\overset{H}{C}{=}O + H_2O$$

Ethyl alcohol Unstable intermediate Acetaldehyde

The unstable intermediates having two OH groups linked to the same carbon atom readily eliminates water.

All aldehydes contain the aldehydic group $-\overset{\diagup H}{C}=O$, and the type formula for all aldehydes is $R-\overset{\diagup H}{C}=O$, where R is an alkyl group, except for the first member of the series, formaldehyde which is $H-\overset{\diagup H}{C}=O$. All ketones contain the ketone group $>C=O$, and the type formula for ketones is $\begin{matrix} R \\ R' \end{matrix}\!\!>C=O$, where R and R′ are identical or differnt alkyl groups:

$CH_3\text{-}CO\text{-}CH_3$	$CH_3\text{-}CO\text{-}C_2H_5$
Dimethyl ketone	Methyl ethyl ketone

The aldehyde and ketone, therefore, both contain the group $>C=O$; this is known as the *carbonyl group*, and this accounts for many similar reactions of aldehydes and ketones.

Formaldehyde, H.CHO. Formaldehyde is formed when calcium formate is heated.

$$\begin{matrix} H.COOCa' \\ + \; HCOOCa' \end{matrix} = H.CHO + CaCO_3 \quad \text{(Ca′ is half-atom of calcium).}$$

It is obtained by catalytic oxidation of methyl alcohol by means of air in contact with heated copper, silver or platinum:

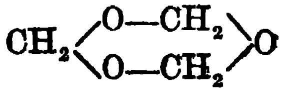
$$CH_3OH + O = HCHO + H_2O.$$

A current of air is bubbled through methyl alcohol taken in a flask, warmed on a waterbath to about 40° ; the mixture of air and alcohol vapour is then passed through a tube containing copper or silver gauze or platinised asbestos, heated to about 500°, and the issuing gas is condensed to a liquid in a flask, cooled in ice. The liquid is a strong solution of formaldehyde in methyl alcohol. The issuing gas may be absorbed in water, giving an aqueous solution of formaldehyde.

An aqueous solution containing 40 per cent formaldehyde and some methyl alcohol (15 per cent) is known as **formalin.**

Properties.—Formaldehyde is a colourless gas with a pungent smell. It may be condensed to a liquid (b.p. −20°). It is soluble in water, alcohol and ether.

Its aqueous solution on evaporation polymerises into a white solid, known as **paraformaldehyde** or **paraform,** $(CH_2O)n$. It reduces Fehling's solution. It gives formaldehyde vapour on heating and hence its use as a fumigant for disinfection. Gaseous formaldehyde on cooling in ice-cold water gives a second polymer, **metaformaldehyde** or **trioxymethylene,** $(CH_2O)_3$. It is a white solid (m.p. 63°) and does not give characteristic aldehyde reactions; but like paraform it gives formaldehyde on heating. It possesses a cyclic structure:



When a solution of formaldehyde is treated with lime water, it slowly polymeries into a mixture of substances, known as *formose,* some of which have the formula $(CH_2O)_6$ or $C_6H_{12}O_6$ and belong to the sugar group. This reaction has a bearing on the synthesis of sugars by plants. Under the influence of sunlight and chlorophyll (green colouring matter of plants) and in presence of moisture, plants feed on carbon dioxide—the carbon being assimilated by plants and converted into carbohydrates, and the oxygen is set free. It is believed that CO_2 is first converted into formaldehyde, which then polymerises into sugar and eventually into starch and cellulose. Formaldehyde has been detected in plant leaves. The conversion of formaldehyde into starch by plants has been observed.

$$(CO_2 + H_2O) \longrightarrow \underset{\text{Formaldehyde}}{CH_2O} \longrightarrow \underset{\text{Sugar}}{(CH_2O)_6} \longrightarrow \underset{\text{Starch/cellulose}}{(C_6H_{10}O_5)}$$

Formaldehyde gives characteristic aldehyde reactions like acetaldehyde, but it *differs* in some respects. This is mentioned under acetaldehyde.

Uses:—Formaldehyde has many uses : (i) It is used as an antiseptic and disinfectant. For disinfection formalin is used in the form of spray or paraform is vaporised over a lamp.

(ii) Formalin is used as a preservative for biological and anatomical specimens. Its use as a preservative for milk is forbidden. A very dilute solution is used as internal antiseptic.

(ii) It hardens glue and gelatin and render them insoluble, and hence its use as a tannin substitute in leather industry. It finds use in making synthetic tannin.

(iii) It is used in making synthetic resins, e.g., *bakelite* (phenol-formaldehyde plastics), *plaskon* (urea-formaldehyde plastics), and *gallalith* (casein plastics). *Bakelite,* a hard infusible resin, (so named after its discoverer Baekeland) is made by heating phenol and formaldehyde in presence of ammonia. It finds use in making electrical insulating materials, phonograph records, fountain pen, etc. *Gallalith* is made by hardening casein (a milk protein) with formaldehyde, and is used as a substitute for ivory, horn, or tortoise shell, and in making buttons.

(iv) It is used in making synthetic dyes, and in making throat lozenge—*formamint* is a mixture of lactose and formaldehyde.

Acetaldehyde, CH_3CHO, is made: (i) by oxidising ethylalcohol with sodium or potassium dichromate and concentrated sulphuric acid, in the laboratory. $CH_3CH_2OH + O = CH_3CHO + H_2O$.

Preparation.—Coarsely powdered sodium dichromate (100 g.) and water (400 c.c.) are placed in a two litre flask fitted with a tap funnel, and attached to a condenser and receiver. Ice-cold water circulates through the condenser and the receiver is cooled in ice. A mixture of absolute alcohol (125 c.c.) and concentrated sulphuric acid (75 c.c.) is slowly run into the flask. The flask is heated on a water bath, and the distillate which contains acetaldehyde and some alcohol and water, collects in the receiver.

The distillate is then taken in a flask fitted with a fractionating column and *gently* warmed from a water bath, when acetaldehyde (b.p. 21°) passes over (leaving alcohol and water behind) and is led into dry ether taken in a wash bottle, cooled in ice.

The ethereal solution is then saturated with *dry* ammonia gas, when crystals of acetaldehyde-ammonia deposit. The crystals are separated and decomposed by distilling with dilute sulphuric acid. The distillate of acetaldehyde is dried over calcium chloride and re-distilled. Pure acetaldehyde is collected in a ice-cold receiver. $CH_3.CHO + NH_3 = CH_3\text{-}CH(OH).NH_2$

$$CH_3CH(OH).NH_2 + H_2SO_4 = CH_3CHO + NH_4HSO_4$$

(ii) by idstilling a dry mixture of calcium acetate and calcium formate.

$$\begin{matrix} CH_3COOCa' \\ +\ HCOOCa' \end{matrix} = CH_3CHO + CaCO_3 \quad (Ca'=\text{a half-atom of calcium}).$$

(iii) by passing vapours of acetic acid and formic acid over a catalyst of manganous oxide, MnO, at 300°.

$$CH_3COOH + HCOOH = CH_3CHO + H_2O + CO_2$$

(iv) by passing a mixture of alcohol vapour and air over copper or silver catalyst at dull red heat. $CH_3CH_2OH + O = CH_3CHO + H_2O$.

(v) by reduction of acetyl chloride by hydrogen in presence of palladium at 150°. $CH_3COCl + H_2 = CH_3CHO + HCl$.

All the above processes illustrate general methods for the preparation of aldehydes.

(vi) by hydration of acetylene by passing into a 20 per cent sulphuric acid containing mercuric sulphate as a catalyst, and kept at about 80°. Acetaldehyde is separated by fractional distillation.

$$CH{\equiv}CH + H_2O = CH_3CHO$$

Methods (iv) and (vi) are used for commercial preparation of acetaldehyde.

Properties.—Acetaldehyde is a colourless gas (b.p. 21°) with a suffocating smell. It is soluble in water, alcohol and ether.

General properties of acetaldehyde and acetone.—The chemical properties of acetaldehyde, CH_3CHO, and acetone, $CH_3\text{-}CO\text{-}CH_3$, are similar in many respects, and this is due to the presence of carbonyl group, $>C{=}O$, in both.

Formaldehyde, H.CHO, also closely resembles acetaldehyde in chemical properties. Their similarities and differences are shown as follows:

(i) **Oxidation :** Aldehydes readily undergo oxidation (with dichromate and sulphuric acid), giving acid with *same* number of carbon atoms. Acetaldehyde gives acetic acid, and formaldehyde formic acid.

$$CH_3CHO + O = CH_3COOH \text{ (acetic acid)}$$

$$H.CHO + O = H.COOH \text{ (formic acid).}$$

Ketone, e.g., acetone, is far less readily oxidised. On drastic oxidation, it gives acid with *fewer* carbon atoms.

$$CH_3\text{-}CO\text{-}CH_3 + 2O_2 = CH_3COOH + CO_2 + H_2O.$$

(ii) **Reduction :** Aldehydes on reduction with sodium amalgam and water, yield *primary* alcohols; acetaldehyde gives ethyl alcohol, and formaldehyde methyl alcohol. $CH_3.CHO + H_2 = CH_3.CH_2OH$

$$H.CHO + H_2 = H.CH_2OH \text{ (methyl alcohol)}$$

A ketone, on being similarly reduced, gives a *secondary* alcohol; acetone gives isopropyl or secondary propyl alcohol.

$$CH_3CO.CH_3 + H_2 = CH_3CH(OH)CH_3 \text{ (isopropyl alcohol)}$$

(iii) **Addition reactions:** (a) Aldehydes and ketones yield the additive compound, cyanhydrin, with hydrocyanic acid, HCN.

$$CH_3CHO + HCN = CH_3CH(OH)CN \text{ (acetaldehyde-cyanhydrin).}$$

$$HCHO + HCN = HCH(OH)CN \text{ (formaldehyde-cyanhydrin)}$$

$$(CH_3)_2CO + HCN = (CH_3)_2C(OH)CN \text{ (acetone-cyanhydrin)}$$

On being shaken with cold saturated solution of sodium bisulphite, $NaHSO_3$, aldehydes and ketones yield bisulphite addition compound.

$$CH_3CHO + NaHSO_3 = CH_3CH(OH)SO_3Na$$
$$HCHO + NaHSO_3 = HCH(OH)SO_3Na$$
$$(CH_3)_2CO + NaHSO_3 = (CH_3)_2C(OH)SO_3Na$$

(c) Acetaldehyde gives acetaldehyde ammonia, a crystalline solid with dry ammonia gas; $CH_3CHO + NH_3 = CH_3CH(OH)NH_2$

Formaldehyde does not form aldehyde-ammonia. With ammonia it gives *hexamethylene tetramine*, $(CH_2)_6N_4$, a colourless crystalline solid, which is used in medicine under the name **hexamine, urotropine** or **aminoform.** $6CH_2O$ (formaldehyde) $+ 4NH_3 = (CH_2)_6N_4 + 6H_2O$

Like acetaldehyde, acetone also forms additive compound with ammonia, but at a low temperature (−65°) only.

$$(CH_3)_2CO + NH_3 = (CH_3)_2C(OH)NH_2 \text{ (acetone-ammonia)}$$

But at ordinary temperature acetone forms a complex substance, *diacetone amine*, with ammonia.

(iv) **Reaction with hydroxylamine,** NH_2OH, (*hydrazine*, $NH_2.NH_2$) and *phenyl hydrazine*, $NH_2.NHC_6H_5$, etc.

(a) Aldehydes and ketones react with hydroxylamine, giving *oximes*, with elimination of water.

$$CH_3CHO + H_2NOH \longrightarrow CH_3CH = NOH \text{ (acetaldoxime)} + H_2O$$
$$HCHO + H_2NOH \longrightarrow HCH{=}NOH + H_2O$$
$$(CH_3)_2CO + H_2NOH \longrightarrow (CH_3)_2C{=}NOH \text{ (acetoxime)} + H_2O$$

(b) Hydrazine reacts similarly with aldehydes and ketones, yielding *hydrazones* with elimination of water.

$$CH_3CHO + H_2N.NH_2 \longrightarrow CH_3.CH{=}N.NH_2 + H_2O$$
$$HCHO + H_2N.NH_2 \longrightarrow H.CH{=}N.NH_2 + H_2O$$
$$(CH_3)_2CO + H_2N.NH_2 \longrightarrow (CH_3)_2C{=}N.NH_2 + H_2O$$

(c) Phenyl hydrazine reacts similarly, giving *phenyl hydrazones* of aldehydes and ketones.

$$CH_3CHO + H_2NNHC_6H_5 \longrightarrow CH_3CH{=}NNHC_6H_5 + H_2O$$
$$HCHO + H_2NNHC_6H_5 \longrightarrow HCH{=}NNHC_6H_5 + H_2O$$
$$(CH_3)_2CO + H_2NNHC_6H_5 \longrightarrow (CH_3)_2C{=}NNHC_6H_5 + H_2O$$

(d) Semicarbazide, $NH_2.NHCONH_2$, reacts with aldehydes and ketones, giving *semicarbazones* which are crystalline and have definite melting points, and hence useful in the identification of aldehydes and ketones.

$$CH_3CHO + H_2N.NHCONH_2 \longrightarrow CH_3CH{=}N.NHCONH_2 + H_2O$$
$$(CH_3)_2CO + H_2N.NHCONH_2 \longrightarrow (CH_3)_2C{=}N.NHCONH_2 + H_2O$$

(v) **Reaction with Grignard reagent:** The aldehyde and ketone form additive compounds with Grignard reagent (such as methyl magnesium bromide, CH_3MgBr), which on hydrolysis yield alcohols. Formaldehyde gives a primary alcohol, acetaldehyde a secondary alcohol and acetone a tertiary alcohol.

$$CH_2 = O \text{ (formaldehyde)} + CH_3MgBr = CH_3CH_2-OMgBr$$
$$CH_3CH_2-OMgBr + H.OH = CH_3CH_2OH + Mg(OH)Br$$
$$CH_3CHO + CH_3MgBr = (CH_3)_2CH-OMgBr$$
$$(CH_3)_2CH-OMgBr + H.OH = CH_3\text{-}CH(OH).CH_3 + Mg(OH)Br$$
$$(CH_3)_2CO + CH_3MgBr = (CH_3)_3C-OMgBr.$$
$$(CH_3)_3\text{-}C\text{-}OMgBr + H.OH = (CH_3)_3C(OH) + Mg(OH)Br$$

Tertiary butyl alcohol.

(vi) **Reaction with PCl_5.** —Aldehydes and ketones react with PCl_5, giving dicholoroparaffins, but no HCl is evolved. Acetaldehyde gives ethylidene chloride, CH_3CHCl_2, and acetone gives $\beta\beta$-dichloropropane, $CH_3.CCl_2.CH_3$.

$$CH_3CHO + PCl_5 = CH_3CHCl_2 + POCl_3.$$
$$CH_3COCH_3 + PCl_5 = CH_3.CCl_2.CH_3 + POCl_3.$$

The dichloroparaffins thus formed, yield back acetaldehyde and acetone on hydrolysis with hot aqueous alkali.

$$CH_3CHCl_2 + 2NaOH = CH_3CHO + 2NaCl + H_2O$$
$$CH_3.CCl_2.CH_3 + 2NaOH = CH_3COCH_3 + 2NaCl + H_2O$$

(vii) **Reaction with alcohol.** —Aldehydes react with alcohol in presence of HCl gas, giving acetals. Acetone does not give acetal.

$$CH_3CHO + 2HOC_2H_5 = CH_3CH.(OC_2H_5)_2 \text{ (acetal)} + H_2O$$
$$HCHO + 2HOCH_3 = H.CH.(OCH_3)_2 \text{ (methylal)} + H_2O$$

(viii) **Reaction with caustic soda or potash.** —Acetaldehyde gives a brown resinous mass, known as *aldehyde-resin*, with caustic alkali. But acetone gives no such resin with caustic alkali. Formaldehyde also gives no resin. When formaldehyde is heated with aqueous caustic alkali, it gives methyl alcohol and formate. One molecule of formaldehyde is reduced to methyl alcohol at the expense of the other which is oxidised to formic acid: **This is Cannizzarro's reaction.**

$$HCHO + HCHO + NaOH = HCH_2OH + HCOONa + H_2O$$

(ix) **Aldol condensation.**—In presence of dilute alkali or aqueous solution of potassium carbonate in the cold acetaldehyde is converted into a syrupy liquid, called *aldol* (which is both aldehyde and alcohol and hence the name *ald* (ehyde-alcoh) *ol*. Aldol is formed by the condensation of two molecules of acetaldehyde. The reaction is called aldol condensation $CH_3CHO + CH_3CHO = CH_3CH(OH)CH_2CHO$ (aldol). Formaldehyde does not give aldol condensation but gives Cannizzaro's reaction in presence of alkali.

The aldol condensation involves the addition of α-hydrogen atoms (i.e., the hydrogen atoms on the carbon atom immediately adjacent to the carbonyl group) on the carbonyl group. If there is no α-hydrogen atoms on the carbon next to carbonyl group, no aldol condensation takes place.

The Cannizzaro's reaction, on the other hand, is given by aldehydes which possess no α-hydrogen atoms. Thus formaldehyde gives Cannizzaro's reaction but fails to undergo aldol condensation.

Acetone, however, undergoes aldol condensation in presence of baryta water, giving diacetone alcohol.

$$(CH_3)_2C = O + H_3C - CO - CH_3 = (CH_3)_2.C(OH).CH_2.CO.CH_3$$

Diacetone alcohol.

(x) **Polymerisation.** —Like formaldehyde (p. 34), acetaldehyde readily polymerises, but acetone does not.

On adding a drop of concentrated sulphuric acid to a solution of acetaldehyde, the latter polymerises into a colourless, pleasant smelling liquid (b.p. 124°), **paraldehyde,** $(CH_3CHO)_3$. It does not give characteristic aldehyde reactions. It has a cyclic structure. It is a soporific. By the action of dilute sulphuric acid upon acetaldehyde at low temperature, a solid polymer, **metaldehyde,** $(CH_3CHO)_n$, is formed. It is used as a fuel (meta fuel). Metaldehyde on distillation with dilute sulphuric acid, gives back acetaldehyde. Therefore, polymerisation of aldehydes is a reversible process.

(xi) **Reducing property.** —Aldehydes are readily oxidised and hence are strong reducing agents. (a) Both acetaldehyde and formaldehyde reduce ammoniacal silver nitrate solution to metallic silver, on warming.

$$CH_3CHO + Ag_2O = CH_3COOH + 2Ag \;;$$

$$H.CHO + Ag_2O = HCOOH + 2Ag$$

(b) Both acetaldehyde and formaldehyde reduce Fehling's solution on boiling, giving a red precipitate of cuprous oxide.

$$CH_3CHO + 2CuO = CH_3COOH + Cu_2O \;;$$

$$HCHO + 2CuO = HCOOH + Cu_2O$$

Fehling's solution contains copper suuphate, caustic soda and sodium potassium tartrate (Rochelle salt), and is deep blue in colour.

Acetone has no reducing property. It does not reduce ammoniacal silver nitrate or Fehling's solution.

(xii) **Action on Schiff's reagent.**—Acetaldehyde and formal dehyde gives purple colour with Schiff's reagent (which is magenta solution made colourless with sulphur dioxide) in the cold. Acetone does not ordinarily restore the colour of Schiff's reagent.

(xiii) **Haloform reaction.**—With bleaching powder solution or chlorine and caustic soda solution both acetaldehyde and acetone give chloroform (p. 21). Similarly, with bromine or iodine and caustic soda, they give bromoform, $CHBr_3$, and iodoform, CHI_3. This is known as *haloform rection.* Formaldehyde does not give this reaction.

$$CH_3CHO + 3NaOCl = CCl_3.CHO + 3NaOH$$

$$CCl_3CHO + NaOH = CHCl_3 + HCOONa$$

Acetone reacts similarly.

Uses of acetaldehyde.—Paralydehyde is a hypnotic. Metaldehyde is used as a fuel. Acetaldehyde is used in the preparation of acetic acid, ethyl alcohol, acetic anhydride, ethylacetate and aldol.

Tests for formaldehyde and acetaldehyde. —Both formaldehyde and acetaldehyde reduce ammoniacal silver nitrate and Fehling's solution, and restore colour of Schiff's reagent. But formaldehyde *differs* from acetaldehyde in its reactions with :

(a) ammonia (p. 37), (b) caustic soda (p. 38) and (c) iodine and caustic soda (p. 39).

Certain colour reactions are also distinctive :

(i) An aqueous solution of formaldehyde gives a rose-red colour, on addition of 2 c.c. of 1% phenyl hydrazine hydrochloride, solution, then 1 c.c. of 5% potassium ferricyanide solution and finally about 5 c.c. strong hydrochloric acid. This is *Schryver's test* for formaldehyde.

(ii) Aqueous formaldehyde develops an intense indigo blue colour, on addition of 1 c.c. of 1% solution of phenyl hydrazine hydrochloride, then 1 c.c. of sodium nitroprusside solution, and finally excess of caustic soda solution.

(iii) Acetaldehyde solution gives a blue colour on the addition of aqueous sodium nitroprusside and piperidine.

(iv) A cherry-red colour develops, on adding sodium nitroprusside solution and an excess of aqueous caustic soda to acetaldehyde solution.

Common reactions and products of acetaldehyde and acetone.—

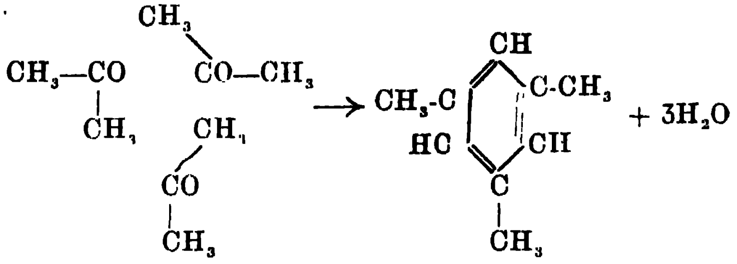
Reagent	Acetaldehyde	Acetone
(i) HCN	Cyanhydrin	Cyanhydrin
(ii) $NaHSO_3$	Bisulphite compound	Bisulphite compound
(iii) NH_2OH	Acetaldoxime	Acetoxime
(iv) NH_2NH_2	Hydrazone	Hydrazone
(v) $NH_2NHC_6H_5$	Phenyl hydrazone	Phenyl hydrazone
(vi) $NH_2NHCONH_2$	Semicarbazone	Semicarbazone
(vii) PCl_5	Ethylidene chloride	$\beta\beta$-dichloropropane
(viii) I_2 & NaOH	Iodoform	Iodoform
(ix) Chlorine	Trichloro acetaldehyde	Trichloro acetone
(x) Aldol condensation	Aldol	Diacetone alcohol

9 **Reactions where acetaldehyde and acetone differ.—**

Reagent	Acetaldehyde	Acetone
(i) Reduction (Na-amalgam+H_2O)	Primary alcohol CH_3CH_2OH	Secondary alcohol CH_3-CH(OH)-CH_3
(ii) Oxidation ($K_2Cr_2O_7+H_2SO_4$)	Acid with *same* number of carbon atoms	Acid with *fewer* carbon atoms, e.g., CH_3COOH
(iii) NH_3	Aldehyde-ammonia	Acetone-amine
(iv) Caustic soda	Aldehyde-resin	No resin
(v) Polymerisation by H_2SO_4	Paraldehyde and metaldehyde	No polymerisation
(vi) Ethyl alcohol	Acetal	No reaction
(vii) Schiff's reagent	Pink colour	No reaction
(viii) Ammonial silver nitrate	Silver mirror	No reaction
(ix) Fehling's solution	Red precipitate	No reaction

Polymerisation.—When acetylene is passed through a red-hot tube, benzene is formed: $3C_2H_2 \longrightarrow C_6H_6$. Such a reaction in which a simple substance is changed into a complex one of the *same empirical formula* but having a molecular weight equal to several multiples of the parent substance, is known as *polymerisation*. The complex substance formed is the *polymer* of the original substance which is called the *monomer*. Polymer has the same empirical formula as the monomer but different molecular formula. Benzene is a trimer of acetylene. Polymerisation is usually reversible, as in the case of polymers of acetaldehyde (p. 39), but this need not be so. Ethylene on polymerisation gives the synthetic resin *polythene*.

Condensation. —When acetone is distilled with concentrated sulphuric acid, it yields mesitylene (trimethyl benczene), a liquid boiling at 163°. Three molecules of acetone interact, with elimination of water and forming mesitylene.



Such a process in which two or more molecules of the same or different substances combine, usually, but not always, with elimination of water, alcohol, HCl, etc., is known as *condensation*, and the substance formed is the *condensation product*—the combination is caused by the union of carbon atoms and hence the condensation product is of stable character. Mesitylene is formed with elimination of water, but in the formation of aldol nothing is eliminated. But in both cases new linkage between carbon atoms of the original molecules develop, and consequently they can not be easily split up into the original molecules.

Acetone, dimethyl ketone, CH_3-$CO.CH_3$, occurs in traces in normal urine, but in the case of diabetic patients, the quantity increases. It also occurs in trace in blood.

Acetone is made commercially: (i) **by dry distillation of calcium acetate.** The method is also suitable for laboratory preparation.

$$\begin{matrix}CH_3COOCa'\\ CH_3.COOCa'\end{matrix}=CH_3COCH_3+CaCO_3 \quad (Ca'=\text{a half-atom of calcium}).$$

Dry calcium acetate (30 g.) is heated first slowly and then strongly in a retort attached to a condenser and receiver (fig. 3). The distillate is crude acetone. It is shaken with saturated solution of sodium bisulphite, when crystalline acetone-bisulphite is deposited. This is filtered and decomposed by distillation with sodium carbonate solution. The acetone passes over. It is dried over calcium chloride and redistilled to get pure acetone.

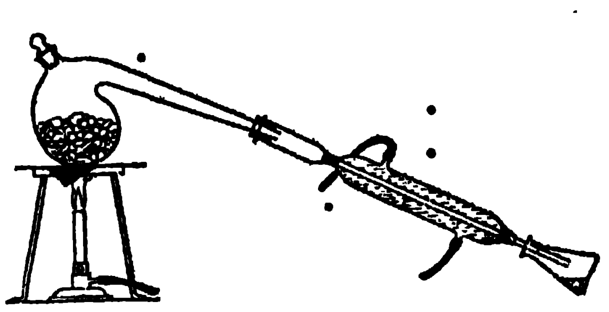


Fig. 3

$$CH_3.CO.CH_3+NaHSO_3 \rightleftharpoons (CH_3)_2.C(OH).SO_3Na$$

$$2(CH_3)_2.C(OH).SO_3Na + Na_2CO_3 = 2(CH_3)_2CO + 2Na_2SO_3 + H_2O + CO_2$$

The calcium acetate (the grey acetate of lime of commerce) is obtained by neutralising the acetic acid of the pyroligneous acid (p. 25) with milk of lime. Acetone is also recovered from crude wood spirit by fractional distillation (p. 25).

(ii) by passing acetic acid vapour over manganous oxide, MnO, catalyst at 300° : $2CH_3COOH = CH_3COCH_3 + CO_2 + H_2O$

(iii) by oxidation of isopropyl alcohol by means of air in presence of heated copper catalyst, or by dehydrogenation by passing over heated copper. $CH_3.CH(OH).CH_3 + O = CH_3.COCH_3 + H_2O$

Isopropyl alcohol, $CH_3.CH(OH).CH_3$, is made by absorption of propylene, $CH_3CH = CH_2$, (from cracked petroleum) in concentrated H_2SO_4, and then hydrolysing the product by heating with dilute H_2SO_4.

$$CH_3\text{-}CH = CH_2 + H_2SO_4 = CH_3.CH(HSO_4)CH_3$$

$$CH_3.CH(HSO_4).CH_3 + H_2O = CH_3.CH(OH).CH_3 + H_2O$$

(iv) by fermentation of starch of maize and rice **(Weizmann process)** in presence of an organism (*Fernbach's bacillus*) which converts the starch mainly into a mixture of butyl alcohol and acetone. The acetone is separated by fractional distillation.

(v) by passing a mixture of ethyl alcohol vapour and steam over a heated catalyst containing iron and calcium :

$$2CH_3CH_2OH + H_2O = CH_3COCH_3 + 4H_2 + CO_2.$$

(vi) by passing a mixture of acetylene and steam over heated zinc oxide catalyst : $2C_2H_2 + 3H_2O = CH_3COCH_3 + 2H_2 + CO_2$.

Properties.—Acetone is a colourless liquid with a pleasant smell (b.p. 56·5°). It is soluble in water, alcohol and ether. Its sp. gr. is 0·792 at 20°.

There are many common reactions of acetone and acetaldehyde ; they have been discussed together under acetaldehyde.

Uses.—Acetone is used as a *solvent* for nitrocellulose in making cordite, and for storing acetylene. It is used in making chloroform, iodoform and sulphonal (a hypnotic), and in spinning cellulose acetate rayon. **Chloretone,** a specific against sea-sickness, is made by the action of potash on a mixture of acetone and chloroform. $(CH_3)_2.CO + CHCl_3 = (CH_3)_2.C(OH).CCl_3$. (chloretone).

Tests.—(i) Like ethyl alcohol acetone gives iodoform reaction with iodine and caustic soda solution (p. 29). But unlike ethyl alcohol, acetone also gives an iodoform reaction with iodine and aqueous *ammonia* (in place of caustic soda). Hence acetone is distinguished from ethyl alcohol.

(ii) A freshly prepared solution of sodium nitroprusside on being added to acetone and then made alkaline with caustic soda. develops an orange red colour (*Legal's test*).

* **Chloral,** trichloroacetaldehyde, $CCl_3.CHO$, is formed by the chlorination of acetaldehyde. $CH_3.CHO + 3Cl_2 = CCl_3.CHO + 3HCl$.

Chloral is made by saturating ethyl alcohol with chlorine first at ordinary temperature, and finally at 90° for several days—chlorine first oxidises the alcohol to acetaldehyde, which is then chlorinated to chloral. $CH_3.CH_2OH + Cl_2 = CH_3.CHO + 2HCl$

$$CH_3.CHO + 3Cl_2 = CCl_3.CHO + 3HCl$$

Chloral is an oily liquid (b.p. 98°) with a penetrating smell (sp. gr. 1·506 at 20°). It closely resembles acetaldehyde in its reactions.

It gives trichloroacetic acid on oxidation with boiling nitric acid.

$$CCl_3.CHO + O = CCl_3.COOH \text{ (trichloroacetic acid).}$$

It is decomposed by hot aqueous alkali, giving chloroform and a formate. $NaOH + CCl_3.CHO = CHCl_3 + HCOONa$.

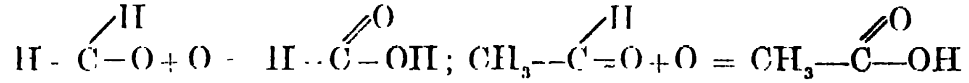
On shaking with one molecular proportion of water chloral gives **chloral hydrate,** $CCl_3.CH(OH)_2$, a crystalline solid, m. .57°, readily soluble in water. Chloral hydrate is a rare exampple of a compound having two OH groups linked to the same carbon atom. Chloral is used in medicine as a soporific.

VIII

FATTY ACIDS

Fatty acids.—Formic acid, HCOOH, and acetic acid, CH_3COOH are the first two members of a series of homologous saturated monobasic acids, known as *fatty acids*. They are so called as two of the higher members—*palmitic acid* and *stearic acid*—are present in animal fats. All acids of the series have the general formula $R\text{-}\overset{O}{\overset{/\!\!/}{C}}\text{-}OH$, where R is an alkyl group, except formic acid which has the formula $H\text{-}\overset{O}{\overset{/\!\!/}{C}}\text{-}OH$. The carboxylic group $\text{—}\overset{O}{\overset{/\!\!/}{C}}\text{-}OH$, is the characteristic of all organic acids. The fatty acids contain one -COOH group and are, therefore, mono carboxylic acids. It is the hydrogen atom of the —COOH group which is replaceable by metals, forming salts.

The formaldehyde, H-CHO, and acetaldehyde, CH_3-CHO, on oxidation give formic and acetic acids respectively



$$H\text{-}\overset{H}{\overset{/}{C}}{=}O + O = H\text{-}\overset{O}{\overset{/\!\!/}{C}}\text{-}OH;\ CH_3\text{—}\overset{H}{\overset{/}{C}}{=}O + O = CH_3\text{—}\overset{O}{\overset{/\!\!/}{C}}\text{—}OH$$

The fatty acids may be regarded as formed by the stepwise oxidation of paraffins. The sequence of the steps are :

Paraffin → Primary alcohol → Aldehyde → Fatty acid

$CH_4 \rightarrow H.CH_2OH \rightarrow H.CHO \rightarrow H.COOH$

$CH_3\text{-}CH_3 \rightarrow CH_3.CH_2OH \rightarrow CH_3.CHO \rightarrow CH_3.COOH$

Formic acid. HCOOH.—Formic acid occurs in the stings of ants, bees and wasps and is partly responsible for the irritating action of their sting. It was first isolated by distilling red ants with water, and hence the name from the Latin *formica*, an ant. Formic acid is formed by: (i) Oxidation of methyl alcohol or formaldehyde by means of air in presence of platinum black:

$$CH_3OH + O = HCHO + H_2O;\ HCHO + O = HCOOH$$

(ii) Hydrolysis of hydrocyanic acid, HCN, by boiling with aqueous caustic soda or strong hydrochloric acid : $HCN + 2H_2O = HCOOH + NH_3$.

(iii) Decomposition of chloroform by heating with alcoholic potash.

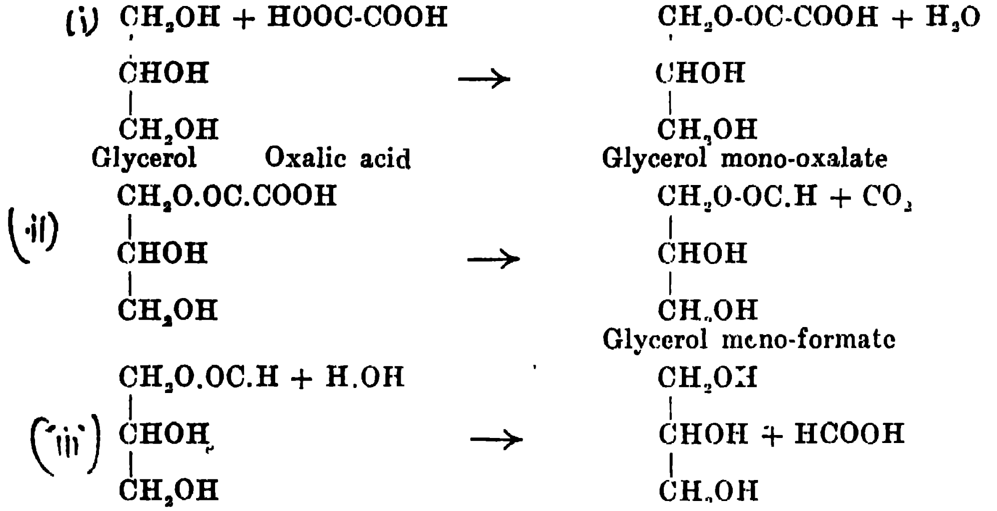
$$CHCl_3 + 4KOH = HCOOK + 3KCl + 2H_2O.$$

Formic acid is prepared: (a) *In the laboratory* by decomposition of oxalic acid in presence of glycerol. When heated alone, oxalic acid decomposes into formic acid and carbon dioxide, but the yield is poor; when heated with glycerol, the yield is much better.

$$HOOC.COOH \text{ (oxalic acid)} = H.COOH + CO_2$$

Glycerine remains unchanged at the end of the action.

The reaction in presence of glycerol is believed to be as follows : Glycerol first reacts with oxalic acid, forming *glycerol mono-oxalate*, which then loses CO_2, giving *glyceryl monoformate*. The monoformate is finally hydrolysed to formic acid and glycerol—the oxalic acid itself acting as a catalyst.



$$\text{(i)}\quad \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + HOOC\text{-}COOH \longrightarrow \begin{array}{l} CH_2O\text{-}OC\text{-}COOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + H_2O$$

Glycerol Oxalic acid Glycerol mono-oxalate

$$\text{(ii)}\quad \begin{array}{l} CH_2O.OC.COOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{l} CH_2O\text{-}OC.H \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + CO_2$$

Glycerol mono-formate

$$\text{(iii)}\quad \begin{array}{l} CH_2O.OC.H \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + H.OH \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + HCOOH$$

Preparation.—Equal weights (50 g.) of oxalic acid and glycerol are heated over a wire gauge in a retort fitted with a condenser and reeciver. The temperature is kept at about 105°-110° until evolution of CO_2 ceases. The liquid is then distilled until the temperature reaches 120°—the distillate is aqueous formic acid.

When larger quantity of formic acid is needed, a further quantity of oxalic acid is added before distillation, and it is decomposed at 105°-110° as before until evolution of CO_2 slackens. The liquid is then distilled.

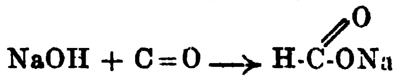
The aqueous solution of formic acid is boiled with excess of litharge and filtered hot—on cooling crystals of lead formate are deposited. $2HCOOH + PbO = (HCOO)_2Pb + H_2O$

The lead formate is dried and then decomposed by passing H_2S over it at about 110°. Anhydrous formic acid passes over and collects in a cooled receiver. $(HCOO)_2Pb + H_2S = 2HCOOH + PbS$.

Concentrated sulphuric acid decomposes formic acid, giving off CO, and hence is unsuitable for its preparation from a formate.

$$HCOONa + H_2SO_4 = NaHSO_4 + CO + H_2O$$

(b) *Industrially* by passing carbon monoxide under a pressure of 5-10 atmospheres over caustic soda at 200° ; sodium formate is thus formed. Dilute H_2SO_4 liberates formic acid from sodium formate.



$$NaOH + C{=}O \longrightarrow H\text{-}\overset{\large O}{\overset{\|}{C}}\text{-}ONa$$

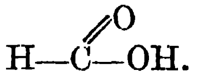
Sodium formate gives pure anhydrous formic acid by distillation with sodium bisulphate. $HCOONa + NaHSO_4 = Na_2SO_4 + HCOOH$.

Properties.—(i) Formic acid is a colourless liquid (b.p. 101°) with a pungent irritating smell. It is highly corrosive and blisters the skin. It is soluble in water, alcohol and ether. It is a fairly strong acid and liberates CO_2 from carbonates. It is a stronger acid than acetic acid. Its salts are soluble in water, except silver and lead formates which are sparingly soluble.

(ii) Formic acid and formates are decomposed by concentrated sulphuric acid, giving off CO. The sulphuric acid acts as a dehydrating agent: $HCOOH = CO + H_2O$.

(iii) Formic acid and formates are *strong reducing agents*. Formic acid reduces ammoniacal silver nitrate solution on warming, depositing metallic silver. $HCOOH + Ag_2O = 2Ag + CO_2 + H_2O$

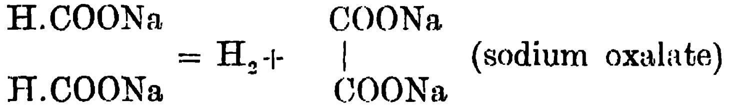
It decolorises acid $KMnO_4$ solution on warming. But it cannot reduce Fehling's solution. The reducing action of formic acid which distinguishes it from acetic acid points to the presence of the aldehyde group in the molecule.



$$H—\overset{\displaystyle O}{\overset{\Vert}{C}}—OH.$$

Its structure shows that it is unique in being both a *carboxylic acid* and an *aldehyde.*

(iv) On heating at 400° sodium formate gives sodium oxalate and hydrogen is evolved. The reaction is used in the manufacture of oxalic acid.



$$\begin{array}{l} H.COONa \\ H.COONa \end{array} = H_2 + \begin{array}{c} COONa \\ | \\ COONa \end{array} \text{ (sodium oxalate)}$$

(v) Formic acid forms esters with alcohols; with ethyl alcohol it gives the ester ethyl formate:

$$H.COOH + HOC_2H_5 \rightleftharpoons HCOOC_2H_5 \text{ (ethyl formate)} + H_2O.$$

(vi) Ammonium formate on heating gives *formamide*:

$$HCOONH_4 = HCONH_2 \text{ (formamide)} + H_2O$$

Uses.—Formic acid is used: (a) in tanning and electroplating, (b) in coagulating rubber latex, and (b) in dyeing wool and cotton.

Acetic acid, CH_3COOH, has long been known under the name of vinegar, and is formed when beer gets sour. The name 'acid' is derived from Latin *acetum*, meaning vinegar.

Acetic acid is *formed* as follows: (i) Hydrolysis of methyl cyanide by heating with aqueous alkali or strong mineral acid.

$$CH_3CN + 2H_2O = CH_3COOH + NH_3$$

In presence of alkali, ammonia is evolved and acetate is formed, but in acid medium free acetic acid and ammonium salt are formed.

(ii) Oxidation of ethyl alcohol by prolonged heating with potassium dichromate and sulphuric acid, or by passing a mixture of the alcohol vapour and air over platinum black at 70°. Acetaldehyde is similarly oxidised.

$$CH_3CH_2OH + O = CH_3CHO + H_2O; \; CH_3CHO + O = CH_3COOH$$

(iii) Sodium methoxide, CH_3ONa, is heated in an atmosphere of cabon monoxide to about 180°. $CH_3.ONa + C = O \longrightarrow CH_3-COONa$

Acetic acid is commonly available in two forms—concentrated acetic acid, alco called *glacial acetic acid*, and dilute acetic acid, known as *vinegar*. Their methods of preparation are different.

Glacial acetic acid is made: (a) Form pyroligneous acid.—The pyroligneous acid (p. 25) is neutralised with milk of lime, and methyl alcohol and acetone are distilled off—the solution of calcium acetate is then evaporated to dryness. The dry calcium acetate (grey acetate of lime) is distilled with concentrated sulphuric acid—the distillate contains about 50% acetic acid.

$$(CH_3COO)_2Ca + H_2SO_4 = CaSO_4 + 2CH_3COOH$$

This is neutralised with caustic soda solution and the solution is evaporated to dryness. The dry sodium acetate thus formed is again distilled with concentrated H_2SO_4—the distillate is glacial acetic acid.

$$2CH_3COONa + H_2SO_4 = 2CH_3COOH + Na_2SO_4$$

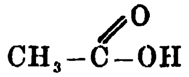
Any water still present is removed by cooling the acid in ice, when pure acetic acid alone solidifies as colourless ice-like (glacial) mass (leaving the water behind), and hence the name *glacial* acetic acid. Pure acetic acid freezes at 16·7° and boils at 119°.

(b) From acetylene.—Acetaldehyde is first made by bubbling acetylene into hot 20% sulphuric acid containing a little mercuric sulphate, at about 70° (p. 16). The acetaldehyde is then oxidised by air at about 60° in presence of manganous acetate which acts as a catalyst. The glacial acetic acid is made by fractional distillation.

$$CH{\equiv}CH + H_2O = CH_3CHO; \; CH_3CHO + O = CH_3COOH$$

Acetic acid can also be obtained by interaction between CH_3OH and CO under high pressure and temperature in presence of catalyst.

$CH_3.OH + C = O.$



$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

Preparation of vinegar.—Vinegar is made by fermentation of weak ethyl alcohol with a microorganism *bacterium aceti* (often called *mother of vinegar*) in presence of air. Air oxidises the alcohol to acetic acid under the influence of an enzyme, present in the organism.

$$CH_3CH_2OH + O \xrightarrow{\text{enzyme}} CH_3COOH + H_2O$$

On exposure to air (in which the vinegar organism is always present), therefore, beer and a weak wine gradually go sour, owing to the formation of acetic acid. Strong wines (containing more than 15% alcohol) such as port and sherry, do not go sour, as the organism cannot survive in strong alcohol.

In the **quick vinegar process** a dilute solution (5-7 per cent) of ethyl alcohol is allowed to trickle over a mass of beech wood shavings contained in a tall wooden vat; the shavings have previously been soaked in vinegar (which contains the vinegar organism) and are, therefore, covered with the mother of vinegar. Air circulates through the vat and oxidises the alcohol as it trickles down, to acetic acid. A plentiful supply of air is essential; with too little air acetaldehyde is formed. The temperature is kept at 35°. The liquid running out below contains 4-6% acetic acid, but by allowing the liquid to trickle a few times through the vat, vinegar containing 14 per cent acetic acid may be made. Vinegar is never used to prepare glacial acetic acid.

Properties.—Acetic is a colourless liquid (b.p. 119°) with a purgent smell (smell of vinegar) and a sharp sour taste. It is corrosive and blisters the skin. At 16·7° it freezes to an ice-like (glacial) mass, called *glacial acetic acid.* It is soluble in water, alcohol and ether. Acetic acid is a useful solvent for many organic compounds, as it is comparatively inert towards oxidising agents.

Reactions :—~~(i)~~ Salt formation : Acetic acid is a weak acid, weaker than the mineral acids HCl, HNO_3 and H_2SO_4. It is also weaker than formic acid. It is a monobasic acid and forms salts, known as *acetates*, by usual methods:

$$CH_3COOH + NaOH = CH_3COONa + H_2O$$

$$2CH_3COOH + Zn = (CH_3COO)_2Zn + H_2$$

~~(ii)~~ Ester formation.—When acetic acid is heated with alcohol, *e.g.*, ethyl alcohol, in presence of a dehydrating agent, usually concentrated H_2SO_4 or HCl gas, an *ester* and water are formed:

$$\text{Acid} + \text{alcohol} \rightleftharpoons \text{ester} + \text{water}$$

$$CH_3COOH + HOC_2H_5 \rightleftharpoons \underset{\text{Ethylacetate}}{CH_3COOC_2H_5} + H_2O$$

The reaction is *reversible*, and the reverse action is known as *hydrolysis*. The dehydrating agents absorb the water formed, and thereby prevent the hydrolysis of the ester.

~~(iii)~~ Action of PCl_5.—Phosphorus pentachloride acts on acetic acid, forming acetyl chloride, CH_3COCl,—the OH group of the acid is replaced by chlorine.

$$CH_3CO.OH + PCl_5 = CH_3COCl + POCl_3 + HCl$$

~~(iv)~~ Action of chlorine.—By direct action of chlorine the hydrogen atoms of the methyl group, $-CH_3$, in CH_3COOH is replaced by chlorine in stages, forming monochloro-, dichloro-, and trichloro- acetic acids.

$$CH_3.COOH + Cl_2 = CH_2Cl.COOH + HCl$$

$$CH_2Cl.COOH + Cl_2 = CHCl_2.COOH + HCl$$

$$CHCl_2.COOH + Cl_2 = CCl_3.COOH + HCl$$

The action is accelerated by sunlight or in presence of red phosphorus or iodine. Bromine reacts similarly, but iodine is without direct action upon acetic acid.

Monochloroacetic acid, $CH_2ClCOOH$, is important in organic synthesis, as the chlorine atom introduced in the CH_3-group shows the reactivity of an alkyl halide :

(a) **Hydrolysis** with moist silver oxide replaces the chlorine atom by OH group, giving hydroxyacetic acid or glycollic acid:

$$CH_2ClCOOH + AgOH = CH_2(OH).COOH + AgCl$$

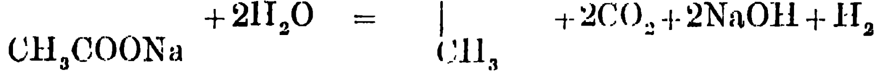
(b) Alcoholic ammonia gives amino-acetic acid or glycine:

$$CH_2ClCOOH + NH_3 = CH_2(NH_2).COOH + HCl$$

(c) Alcoholic potassium cyanide gives cyanoacetic acid.

$$\underset{\text{potassium chloroacetate}}{CH_2Cl.COOK} + KCN = \underset{\text{potassium cyanoacetate}}{CH_2(CN).COOK} + KCl$$

(v) **Formation of ethane.**—An aqueous solution of sodium (or potassium) acetate yields, on electrolysis, a mixture of ethane and CO_2 at the anode, and caustic soda (or potash) and hydrogen at cathode. This is *Kolbe's method.*



$$\begin{array}{l} CH_3COONa \\ CH_3COONa \end{array} + 2H_2O = \begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} + 2CO_2 + 2NaOH + H_2$$

(vi) **Formation of methane.**—Sodium acetate on heating with soda-lime, gives methane. $CH_3COONa + NaOH = CH_4 + Na_2CO_3$

(vii) **Formation of acetamide.**—Ammonium acetate on heating gives acetamide, CH_3CONH_2

$$CH_3COONH_4 = CH_3CONH_2 + H_2O$$

(viii) **Formation of acetaldehyde and acetone.**—A mixture of calcium acetate and calcium formate yields acetaldehyde, on heating (p. 35). Heating calcium acetate alone gives acetone (p. 41).

(ix) **Formation of acetic anhydride.**—A mixture of sodium acetate and acetyl chloride gives acetic anhydride, on heating.

$$CH_3CO.ONa + ClCOCH_3 = \underset{\text{Acetic anhydride}}{CH_3CO.O.COCH_3} + NaCl$$

The reactions of acetic acid are typical of the fatty acids.

Uses of acetic acid.—Acetic acid is used: (i) in the preparation of acetates, acetic anhydride, acetyl chloride, acetone and ethyl acetate, (ii) in making cellulose acetate rayon, (iii) in coagulating rubber latex, and (iv) in curing meat and fish. It is an important laboratory reagent and also a solvent. A mixture of glacial acetic acid and chromic oxide, CrO_3, is a powerful oxidising agent.

The acetates.—The acetates (the normal salts of acetic acid) are mostly crystalline solids which are soluble in water. Sodium and potassium acetates are often used in organic reactions to convert a mineral acid into weaker organic acid. $CH_3COONa + HCl \rightleftharpoons CH_3COOH + NaCl$.

Basic acetate of copper (*verdigris*) is a green pigment. Basic lead acetate, called *sugar of lead* because of its sweet taste, is used in medicine. ***Paris green*** (a mixture of copper acetate and copper arsenite) is an insecticide. Acetates of iron and aluminium are used as ***mordants*** (i.e., substances which serve to attach the dye 'fast' to the cloth) in dyeing cotton cloth. The cloth is steeped in iron (or aluminium) acetate solution and then steamed, when the acetates are hydrolysed—the acetic acid is driven off and the hydroxides of Fe and Al are deposited on the fibre, where they combine with the dye and finally fix it.

Distinctive tests for formic and acetic acids.—

Dry tests : Use solid sodium formate and acetate.

Reagent	Formic acid	Acetic acid
(i) Dilute H_2SO_4. Warm	Pungent smell of formic acid	Smell of vinegar
(ii) Conc. H_2SO_4. Warm	CO is given off; burns with blue flame	Smell of vinegar
(iii) Ethyl alcohol +conc. H_2SO_4; Warm	CO is given off	Fruity smell of ethyl acetate
(iv) Arsenious oxide. Heat*	No action	Nauseating smell of cacodyl oxide.

* **Cacodyl oxide test.** —On heating *dry* acetate with a little arsenious oxide, As_2O_3, a nauseating smell of cacodyloxide is produced.

Wet tests : Use neutral aqueous solutions of sodium formate and acetate.

Reagent	Formic acid	Acetic acid
(i) $FeCl_3$ solution	Deep red colour	Deep red colour
(ii) $AgNO_3$ solution	White precipitate, blackens on heating	White precipitate
(iii) $HgCl_2$ solution	White precipitate of Hg_2Cl_2	No change
(iv) Acid $KMnO_4$ soln.	Decolorises	No change

General methods of preparation of fatty acids.—

(i) Oxidation of primary alcohol gives acid with the *same* number of carbon atoms. $R.CH_2OH + O_2 = R.COOH + H_2O$

(ii) Hydrolysis of alkyl cyanide with boiling alkali or mineral acids.

$$R.CN + H_2O + NaOH = R.COONa + NH_3$$

$$R.CN + 2H_2O + HCl = R.COOH + NH_4Cl$$

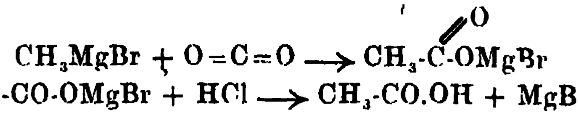
(iii) Hydrolysis of esters with acids or alkalis. The alkaline hydrolysis of esters is called **saponification.** $RCOOCH_3 + NaOH = RCOONa + CH_3OH$.

Higher fatty acids, e.g., palmitic and stearic acids, are obtained from fats and oils by this process.

(iv) Heating a dicarboxylic acid having two -COOH groups linked to the same carbon atom. $HOOC\text{-}COOH$ (oxalic acid) $= H.COOH + CO_2$

$HOOC\text{-}CH_2\text{-}COOH$ (malonic acid) $= CH_3.COOH + CO_2$.

(v) **Grignard synthesis of acid.**—In this process CO_2 is passed into a mixture of alkyl halide and Mg in *dry* ether medium, and then the mixture is acidified with HCl, e.g. $CH_3Br + Mg = CH_3MgBr$



$$CH_3MgBr + O{=}C{=}O \longrightarrow CH_3\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OMgBr$$

$$CH_3\text{-}CO\text{-}OMgBr + HCl \longrightarrow CH_3\text{-}CO.OH + MgBrCl$$

The methods (ii) and (v) offer routes for preparing acids from *lower* alcohols, since the alcohols may be readily converted into alkyl halides (p. 17), e.g.,

$$CH_3OH \xrightarrow{\text{red P \& Br}} CH_3Br \xrightarrow{KCN} CH_3CN \xrightarrow{H_2O} CH_3COOH.$$

IX

DERIVATIVES OF ACIDS

Acid or acyl chlorides, $R\text{-}\overset{''}{C}\text{-}Cl$, may be regarded as acids in which the OH of the -COOH group is replaced by a chlorine atom. Acid chlorides may be formed by the action of phosphorus tri or pentachloride or thionyl chloride, $SOCl_2$, upon a fatty acid:

$$3R.COOH + PCl_3 = 3R.CO.Cl + H_3PO_3.$$

The reaction with acetic acid gives acetyl chloride, CH_3COCl.

$$3CH_3COOH + PCl_3 = 3CH_3COCl + H_3PO_3.$$

$$CH_3COOH + PCl_5 = CH_3COCl + POCl_3 + HCl.$$

$$CH_3COOH + SOCl_2 = CH_3COCl + SO_2 + HCl.$$

Acetyl chloride, CH_3COCl, is the most important acid chloride; CH_3CO- is the acetyl group. *Formyl chloride,* $HCOCl$, *is unknown.*

Acetyl chloride, CH_3COCl, is formed by the action of phosphorus tri- or penta- chloride, or thionyl chloride on glacial acetic acid.

Preparation.—Phosphorus trichloride (40 g.) is slowly added from a tap funnel to glacial acetic acid (50 g.) taken in a distilling flask fitted with a condenser and receiver. The receiver is attached to a soda lime tower to absorb hydrogen chloride fumes. The flask is gently warmed on a water bath to 40°—50°. As soon as the evolution of hydrogen chloride slackens, the water bath is heated to boiling, when acetyl chloride distils at 55°.

Properties. —Acetyl chloride is a colourless fuming liquid (b.p. 55°) with a pungent smell, and strongly fumes in moist air. Its chemical reactions are:

(i) **Hydrolysis:** It is vigoroulsy decomposed by water, giving acetic acid. $CH_3COCl + HOH = CH_3COOH + HCl$.

(ii) **Alcoholysis:** It reacts with alcohol, giving esters; ethyl alcohol yields ethyl acetate, $CH_3COOC_2H_5$.

$$CH_3CO.Cl + H.OC_2H_5 = CH_3COOC_2H_5 + HCl$$

The univalent actyl group, CH_3CO-, replaces the H atom of the hydroxyl group of the alcohol, yielding the acetyl derivative. Thus acetyl chloride is used to *detect* and *estimate* the hydroxyl group in organic compounds. The process is known as **acetylation.**

(iii) **Ammonolysis:** It reacts with ammonia, forming acetamide.

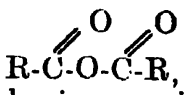
$$CH_3CO.Cl + H.NH_2 = CH_3CONH_2 \text{ (acetamide)} + HCl.$$

Acetyl chloride also reacts with compounds containing $-NH_2$ and $=NH$ groups, giving acetyl derivatives.

$$CH_3COCl + \underset{\text{Methylamine}}{H_2N.CH_3} = \underset{\text{Methyl acetamide}}{CH_3CONHCH_3} + HCl$$

$$CH_3COCl + \underset{\text{Dimethylamine}}{HN(CH_3)_2} = \underset{\text{Dimethyl acetamide}}{CH_3CON(CH_3)_2} + HCl$$

(iv) **Reduction:** It is reduced to acetaldehyde by hydrogen in presence of palladium at 150°. $CH_3COCl + H\text{-}H = CH_3\text{-}CHO + HCl$.



Acid anhydrides, $R\text{-}\overset{O}{\overset{/\!/}{C}}\text{-}O\text{-}\overset{O}{\overset{/\!/}{C}}\text{-}R$, may be regarded as derived from vo molecules of monobasic organic acids by elimination of a molecule of water. $R\text{-}CO\text{-}OH + HO\text{-}OC\text{-}R = R\text{-}CO\text{-}O\text{-}OC\text{-}R + H_2O$.

But they are commonly made by heating an acid chloride with sodium salt of the acid.

$$R\text{-}CO\text{-}Cl + NaO\text{-}OC\text{-}R = R\text{-}CO\text{-}O\text{-}OC\text{-}R + NaCl.$$

Acetic anhydride, $CH_3CO\text{-}O\text{-}COCH_3$, is made by heating anhydrous sodium acetate with acetyl chloride.

$$CH_3COONa + ClCOCH_3 = CH_3CO.O.COCH_3 + NaCl.$$

Preparation.—Fused sodium acetate (50 g.) is placed in a retort fitted with a condenser and receiver, and acetyl chloride (40 g.) is slowly run in from a tap funnel, the retort being cooled under water. When all the acetyl chloride has been added, the mixture is well stirred and then distilled. Acetic anhydride distils between 135°-140°.

Properties. —Acetic anhydride is a colourless liquid (b.p. 137°) with an irritating smell. It does not fume in moist air, It resembles acetyl chloride in chemical properties, being acted on by water, alcohol, and ammonia, and amines (containing $-NH_2$ and $=NH$ groups) though less rapidly.

Hydrolysis: $CH_3CO.O.COCH_3 + H.OH = CH_3COOH + CH_3COOH$

Alcoholysis: $CH_3CO.O.COCH_3 + H.OC_2H_5 = CH_3COOC_2H_5 + CH_3COOH$

Ammonolysis: $CH_3CO.O.COCH_3 + H.NH_2 = CH_3CONH_2 + CH_3COOH$.

Like acetyl chloride, acetic anhydride may be used for the detection of hydroxyl groups. It is a more convenient reagent for acetylation than acetyl chloride.

Uses.—Acetic anhydride is used in making aspirin, but it is largely consumed n producing cellulose acetate for artificial silk.

Acetic anhydride is made **commercially :**

(i) *by dehydrating glacial acetic acid* by passing its vapour over a catalyst of dium ammonium phosphate and boron phosphate kept at 600°.

$$CH_3COOH + HOOCCH_3 = CH_3CO.O.OCCH_3 + H_2O.$$

(ii) *by passing ketene into glacial acetic acid,*

$$CH_2{=}C{=}O + CH_3COOH = CH_3CO.O.OCCH_3$$

etene, $CH_2{=}C{=}O$, a gas, is made by thermal decomposition of acetone at 600°.

$$CH_3COCH_3 \longrightarrow CH_2{=}C{=}O + CH_4.$$

(iii) *by passing acetylene into glacial acetic acid* in presence of mercuric sulphate catalyst, when ethylidene diacetate is formed. It is decomposed by heat into acetaldehyde and acetic anhydride.

$CH{\equiv}CH + CH_3COOH \longrightarrow CH_3CH.(OCOCH_3)_2$ (Ethylidene diacetate)

$CH_3CH.(OCOCH_3)_2 \longrightarrow CH_3CHO + CH_3CO.O.COCH_3$.

Acetamide, CH_3CONH_2, is formed by the action of ammonia on acetyl chloride, on acetic anhydride and on esters of acetic acid, e.g., ethyl acetate. $CH_3COCl + HNH_2 = CH_3CONH_2 + HCl$

$$CH_3CO.O.COCH_3 + HNH_2 = CH_3CONH_2 + CH_3COOH$$

$$CH_3COOC_2H_5 + HNH_2 = CH_3CONH_2 + C_2H_5OH$$

It is usually prepared by melting ammonium acetate by heat and then distilling the product. $CH_3COONH_4 = CH_3CONH_2 + H_2O$.

Properties.—Acetamide is a colourless crystalline solid (m.p. 92°; b.p. 222°), soluble in water, alcohol and ether. The aqueous solution is neutral to litmus. Pure acetamide is odourless, but the impure product has a strong smell of mice.

Chemical properties.—(i) Hydrolysis: Acetamide is hydrolysed by boiling mineral acids or alkalis, giving acetic acid and ammonia or their salts. $CH_3CONH_2 + H_2O + HCl = CH_3COOH + NH_4Cl$

$$CH_3CONH_2 + NaOH = CH_3COONa + NH_3.$$

(ii) Action of nitrous acid: Reaction with nitrous acid gives acetic acid and evolves nitrogen.

$$CH_3CONH_2 + ON.OH = CH_3COOH + N_2 + H_2O.$$

(iii) **Dehydration** by heating with P_2O_5 gives methyl cyanide or acetonitrile. $CH_3CONH_2 = CH_3CN + H_2O$.

(iv) **Hofmann reaction:** Acetamide reacts with a solution of sodium hypochlorite or hypobromite and caustic soda, giving methyl amine, CH_3NH_2. The reaction involves elimination of a carbon atom as carbon dioxide.

$$CH_3CONH_2 + NaOCl + 2NaOH = CH_3NH_2 + NaCl + Na_2CO_3 + H_2O$$

XX. **Methyl cyanide, acetonitrile,** CH_3CN, is a colourless, poisonous liquid (b.p. 82°) with a ethereal smell, and is sparingly soluble in water. It is formed by :

(i) distilling acetamide with phosphorus pentoxide.

(ii) heating methyl iodide with an alcoholic solution of potassium cyanide. $CH_3I + KCN = CH_3CN + KI$.

(iii) dehydrating acetoxime with acetic anhydride.

$$CH_3CH{=}NOH \text{ (acetoxime)} = CH_3CN + H_2O.$$

Acetaldehyde reacts with hydroxylamine, NH_2OH, giving acetoxime. $CH_3CHO + H_2NOH \longrightarrow CH_3CH{=}NOH + H_2O$.

Reactions.—(i) Hydrolysis: In presence of strong HCl or moderately strong H_2SO_4, methyl cyanide undergoes partial hydrolysis to acetamide, and finally to acetic acid, on boiling the solution.

$$CH_3CN + H_2O = CH_3CONH_2$$

$$CH_3CONH_2 + H_2O + HCl = CH_3COOH + NH_4Cl$$

Hydrolysis by boiling alkali evolves ammonia:

$$CH_3CN + H_2O + NaOH = CH_3COONa + NH_3$$

The relation between acetonitrile, acetamide, and ammonium acetate is as follows :

$$\underset{\text{Ammonium acetate}}{CH_3COONH_4} \underset{H_2O}{\overset{\text{Heat}}{\rightleftharpoons}} \underset{\text{Acetamide}}{CH_3CONH_2} \underset{H_2O}{\overset{P_2O_5}{\rightleftharpoons}} \underset{\text{Acetonitrile}}{CH_3CN}$$

(ii) *Reduction* by hydrogen in presence of nickel at 180° or by sodium and alcohol gives ethylamine. $CH_3CN + 2H_2 = CH_3CH_2NH_2$ (ethylamine)

Esters. —When an alcohol reacts with an organic or inorganic acid, an ester and water are formed, just as an alkali acts on an acid to give salt and water. Acid + alcohol $\rightleftharpoons$ Ester + water

$$\underset{\text{Acetic acid + Ethyl alcohol}}{CH_3COOH + C_2H_5OH} \rightleftharpoons \underset{\text{Ethyl acetate + water}}{CH_3COOC_2H_5 + H_2O}$$

$$(\text{cf. } CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O).$$

$$C_2H_5OH + \underset{\text{Nitric acid}}{HO.NO_2} = \underset{\text{Ethyl nitrate}}{C_2H_5ONO_2} + H_2O.$$

Esters may be looked upon as acids in which the acid hydrogen, i.e., replaceable hydrogen atom, has been changed for an alkyl group, just as a salt is formed by replacing the acid hydrogen by a metal. But it must be made clear that alcohols are not bases, nor are esters salts.

Ethyl acetate, $CH_3COOC_2H_5$ is made: (i) by heating ethyl alcohol and acetic acid in presence of concentrated sulphuric acid which acts as a dehydrating agent.

Preparation.—Equal volumes of ethyl alcohol and concentrated sulphuric acid are taken in a distilling flask fitted with a condenser and a receiver, and the mixture heated on a oil bath to 140°. A mixture of equal volumes of glacial acetic acid and ethyl alcohol is run in from a tap funnel at the same speed as the liquid distils over into the receiver. The distillate contains ethyl acetate and some alcohol, acetic acid and water. It is shaken with sodium carbonate solution when the acid is neutralised. The aqueous layer is separated from the upper oily layer of the ester. The oil is then shaken with sodium chloride solution when alcohol passes into the aqueous layer, and is separated. The oil is then dried over calcium chloride and distilled from a water bath. Ethyl acetate boils at 77°.

(ii) by boiling under reflux (fig. 4) a mixture of ethyl alcohol (which has been saturated with hydrogen chloride gas) and acetic acid for about half an hour and pouring the product into sodium chloride solution **(Fischer-Speier method).** The ester separates as an oil, which is purified as above. HCl acts partly as a dehydrating agent and partly as a catalyst.

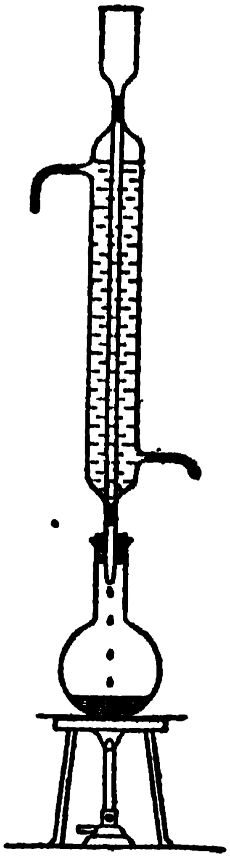


Fig. 4

(iii) by the action of ethyl iodide on silver acetate.

$$CH_3COOAg + IC_2H_5 = CH_3COOC_2H_5 + AgI.$$

(iv) by the action of acetyl chloride or acetic anhydride on ethyl alcohol.

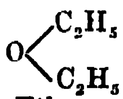
$$CH_3COCl + HOC_2H_5 = CH_3COOC_2H_5 + HCl.$$

Ethyl acetate is now made commercially from acetaldehyde in presence of aluminium ethylate as a catalyst.

$$2CH_3CHO = CH_3COOC_2H_5.$$

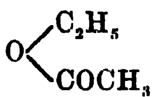
Properties. —Ethyl acetate is a colourless neutral liquid with a pleasant, fruity smell, b.p. 77°. It is lighter than water (sp. gr. 0·9 at 20°) and sparingly soluble in it. It is soluble in alcohol and ether.

In point of structure and in chemical behaviour it stands between very stable ether and unstable acetic anhydride.



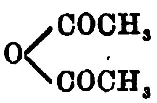
$O\begin{matrix}\diagup C_2H_5\\ \diagdown C_2H_5\end{matrix}$

Ether



$O\begin{matrix}\diagup C_2H_5\\ \diagdown COCH_3\end{matrix}$

Ethyl acetate



$O\begin{matrix}\diagup COCH_3\\ \diagdown COCH_3\end{matrix}$

Reactions,—(i) **Hydrolysis:** Ethyl acetate is slowly decomposed by hot water into ethyl alcohol and acetic acid, but much more rapidly in presence of mineral acids or caustic alkali.

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

$$CH_3COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH.$$

Hydrolysis of an ester in presence of alkali, giving salt of the acid and alcohol, is known as **saponification.**

(ii) **Ammonolysis:** Ammonia reacts, giving acetamide and ethyl alcohol. $CH_3COOC_2H_5 + HNH_2 = CH_3CONH_2 + C_2H_5OH$

(iii) **Alcoholysis**: It reacts with another alcohol, e.g., CH_3OH, giving ester of the added alcohol, e.g., methyl acetate, CH_3COOCH_3.

$$CH_3COOC_2H_5 + HOCH_3 = CH_3COOCH_3 + C_2H_5OH$$

(iv) **Reduction to alcohol:** It is reduced to alcohol (a) with nascent hydrogen by the action of sodium and alcohol **(Bouveault—Blanc reaction),** (b) by the action of hydrogen at high pressure (200 atmospheres) and temperature (250°) in presence of copper chromite catalyst.

$$CH_3COOC_2H_5 + 2H_2 = CH_3CH_2OH + C_2H_5OH$$

Ester reduction offers a method to convert a fatty acid, R.COOH, into a primary alcohol, $R.CH_2OH$; in the above instance CH_3COOH (as ethyl acetate) is reduced to CH_3CH_2OH.

(v) **Reaction with PCl_5** yields acetyl chloride and ethyl chloride.

$$CH_3COOC_2H_5 + PCl_5 = CH_3COCl + POCl_3 + C_2H_5Cl$$

An ester is generally **identified** by separating and identifying the alcohol and acid formed on hydrolysis of an ester with hot aqueous alkali.

Ethyl acetate is used as a solvent for nitro-cellulose in the preparation of photographic films, and in essences. A good stimulent, it finds use in medicine.

Many esters occur in fruits, flowers and other parts of plants, and it is to their presence generally that the sweet smell of the part is due. On account of their sweet scent they are prepared artificially and used as substitutes for natural perfumes and fruit essences. Ethyl formate is used as a constituent of artificial rum flavour. Ethyl butyrate occurs in pineapples. Amyl butyrate possesses an apricot flavour. Octyl acetate is present in oranges. Amyl acetate has a smell of pears and is used in making artificial banana oil. Many esters, such as amyl acetate and butyl acetate, are used as solvents, mainly for lacquers.

Esters of nitrous acid and nitroparaffin. —The alkyl nitrites are isomeric with nitroparaffins. Both have the general formula $R.NO_2$, but they differ in structure:

$$R-O-N=O \text{ (alkyl nitrite)} \qquad R-NO_2 \text{ (nitroparaffin).}$$

Ethyl nitrite and nitroethane are isomeric, so are also methyl nitrite and nitromethane. Their structures are as follows:

Ethyl nitrite, C_2H_5-O=NO, b.p. 16° **Nitroethane, $C_2H_5.NO_2$, b.p. 114°**
Methyl nitrite, CH_3-O=NO, b.p. −12° **Nitromethane, CH_3NO_2, b.p. 101°.**

The nitroparaffins may be looked upon as paraffins in which a hydrogen atom is replaced by a nitro group, $-NO_2$. They are sweet smelling liquids, having boiling points higher than the isomeric alkyl nitrites. Nitroparaffins are prepared by distilling alkyl iodide with silver nitrite. Ethyl iodide gives nitroethane.

$$C_2H_5I + AgNO_2 = C_2H_5NO_2 + AgI$$

Nitrites are made by the action of nitrous acid on the alcohol. Ethyl nitrite is obtained by the action HCl on a mixture of ethyl alcohol and sodium nitrite, when nitrous acid is liberated.

$$C_2H_5OH + HO.NO \longrightarrow C_2H_5ONO + H_2O$$

Chemically, they are distinguished by reaction with:

(i) **Aqueous caustic alkali:** Alkyl nitrite is hydrolysed by the alkali, while the nitroparaffin dissolves in the alkali, forming a salt.

Ethyl nitrite $C_2H_5ONO + NaOH = C_2H_5OH + NaNO_2$

Nitro ethane $C_2H_5NO_2 + NaOH = C_2H_4NaNO_2$ (sodium nitro ethane) $+ H_2O$

(ii) **Reduction with nascent hydrogen:** Alkyl nitrite gives alcohol and hydroxylamine, NH_2OH, while nitroparaffin gives a primary amine.

Ethyl nitrite $C_2H_5ONO + 4H = C_2H_5OH + NH_2OH$

Nitroethane $C_2H_5NO_2 + 6H = C_2H_5NH_2 + 2H_2O$

Both ethyl nitrite and amyl nitrite are used in medicine in case of heart disease, as they cause relaxation of muscles and expansion of blood vessels.

Glycine, glycocoll, aminoacetic acid, $CH_2(NH_2)COOH$, is present in the urine of horse as hippuric acid or benzoyl glycine, $C_6H_5CO.NHCH_2COOH$. It is made by the action of alcoholic solution of ammonia on chloroacetic acid, $CH_2ClCOOH$.

$$CH_2ClCOOH + 3NH_3 = CH_2(NH_2)COONH_4 + NH_4Cl$$

The aqueous solution of the ammonium salt of glycine is boiled with copper carbonate and filtered—the filtrate on cooling deposits sparingly soluble *deep blue* crystals of copper salt of glycine. Glycine is obtained by passing H_2S through the hot solution of this salt, filtering from copper sulphide, and concentrating the solution.

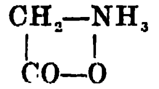
$$(CH_2NH_2COO)_2Cu + H_2S = 2CH_2NH_2COOH + CuS$$

Glycine is a colourless crystalline solid, soluble in water. It has a sweet taste. Its aqueous solution gives a deep-red colour with ferric chloride solution. Glycine contains a -COOH group and hence possesses *acidic* properties, and a primary amino group, $-NH_2$, which confers *basic* properties. It is, therefore, neutral to litmus. Being amphoteric in nature, it forms salts with both acids and bases. $H_2NCH_2COOH + HCl = HCl.H_2NCH_2COOH$ Glycine hydrochloride.

$$H_2NCH_2COOH + NaOH = H_2NCH_2COONa + H_2O$$

sodium aminoacetate

It forms an internal salt with itself, e.g.,



$$\begin{array}{l} CH_2\text{—}NH_3 \\ \,|\qquad\;\; | \\ CO\text{—}O \end{array}$$

It acts like a primary amine in its reaction with nitrous acid, giving off nitrogen. $HONO + H_2NCH_2COOH = (HO)CH_2COOH + N_2 + H_2O$

It gives methylamine on heating with soda lime:

$$CH_2(NH_2)COOH = CH_3NH_2 + CO_2.$$

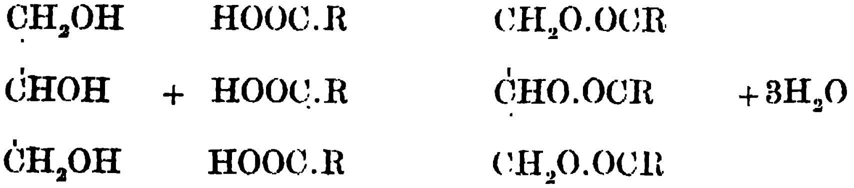
Alanine, α-aminopropionic acid, $CH_3CH(NH_2)COOH$, is another amino acid, and resembles glycine in chemical behaviour. The amino acids are of great interest in relation to *proteins* which are complex nitrogenous organic substances present in animal and vegetable tissues. Protein is an indispensable article of our diet. Protein on hydrolysis yields a mixture of amino acids. Our knowledge of proteins is mainly due to the pioneer work of Emil Fischer.

X

OILS, FATS AND GLYCEROL

Fats and oils. —Fats and oils are glyceryl esters of fatty acids (usually of high molecular weight such as palmitic acid, $CH_3\text{-}(CH_2)_{14}\text{-}COOH$, and stearic acid, $CH_3\text{-}(CH_2)_{16}\text{-}COOH$.

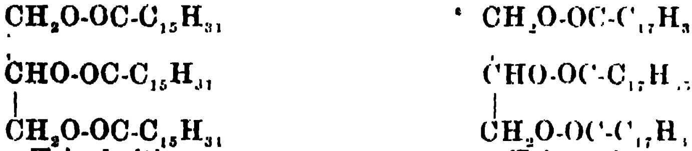
Glycerol is a trihydric alcohol and reacts with a fatty acid, RCOOH, yielding glycerol esters, known as *glycerides*.



$$\begin{array}{lclcl} CH_2OH & & HOOC.R & & CH_2O.OCR \\ | & & & & | \\ CHOH & + & HOOC.R & & CHO.OCR \quad +3H_2O \\ | & & & & | \\ CH_2OH & & HOOC.R & & CH_2O.OCR \end{array}$$

The glycerides are named as follows : *tristearin* (tristearic ester of glycerol), *tripalmitin* (tripalmitic ester of glycerol), and *triolein* (trioleic ester of glycerol), etc. Stearic and palmitic acids are *saturated* fatty acids; oleic acid, $CH_3\text{-}(CH_2)_7\text{-}CH = CH\text{-}(CH_2)_7\text{-}COOH$, contains two hydrogen atoms less than stearic acid and is called an *unsaturated fatty acid*.

The formula for tripalmitin and tristearin are :



$$\begin{array}{lcl} CH_2O\text{-}OC\text{-}C_{15}H_{31} & \qquad & CH_2O\text{-}OC\text{-}C_{17}H_{35} \\ | & & | \\ CHO\text{-}OC\text{-}C_{15}H_{31} & & CHO\text{-}OC\text{-}C_{17}H_{35} \\ | & & | \\ CH_2O\text{-}OC\text{-}C_{15}H_{31} & & CH_2O\text{-}OC\text{-}C_{17}H_{35} \end{array}$$

Tripalmitin Tristearin

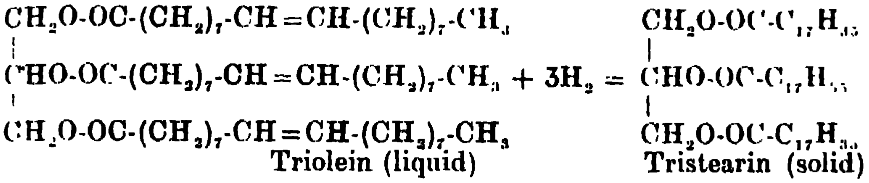
Stearin (m.p. 71°) and palmitin (m.p. 60°) are solids, while olein, an unsaturated glyceride (m.p. 17°) is a liquid at the ordinary temperature. The glycerides of saturated fatty acids are generally solids, whereas the glycerides of unsaturated fatty acids liquids. Stearin, palmitin and olein constitute the main bulk of fats in food and in body fat. The animal fats beef, mutton tallow and lard chiefly consist of the above glycerides. Palmitin is the main constituent of palm oil, and olein of olive oil.

Fats and oils are lighter than water and are insoluble in it. They are, however, soluble in organic solvents such as carbon tetrachloride, benzene, acetone, ether, etc. The fats and oils are obtained from both vegetable and animal sources. Animal fats are obtained by boiling the chopped animal tissues with water, when the fat separates as a top layer. The vegetable oils, e.g., olive oil, linseed oil, groundnut oil, etc., are extracted by mechanically crushing and pressing the seeds or fruits of certain plants. Alternatively, they can be extracted by solvents such as benzene, carbon tetrachloride, etc. The vegetable oils have relatively low melting points and are usually liquids in comparison to animal fats, because the former contain a high proportion of unsaturated glycerides.

There is no difference between fats and oils; the fats are solids at the ordinary temperature, whereas the oils are liquids. Cocoanut oil is usually a fat in temperate zone and an 'oil' in tropics. In our country cocoanut oil is a fat in winter and an oil in summer.

Certain vegetable oils such as linseed oil and tung oil, slowly absorb oxygen from the air and change into a resinous film, when spread in thin layers on some surface such as wood which is exposed to air. They are called *drying oils* and are used in making oil-paints (which are suspensions of pigments in linseed oil usually). Oil cloth is made by covering cloth with linseed oil and allowing it to dry in air.

Hydrogenation of oils.—The chief difference between an oil and a fat is that the oil contains a greater proportion of *unsaturated* glycerides such as triolein, etc. The glycerides of *saturated* fatty acids are mostly solid fats which are in great demand for the preparation of soaps and candles, and as a butter substitute. Now, oleic acid contains two atoms of hydrogen less than stearic acid, and the unsaturated glyceride, triolein, a liquid, may be reduced to tristearin, a solid, by the action of hydrogen in presence of nickel catalyst.



$$\begin{array}{lcl} CH_2O\text{-}OC\text{-}(CH_2)_7\text{-}CH=CH\text{-}(CH_2)_7\text{-}CH_3 & & CH_2O\text{-}OC\text{-}C_{17}H_{35} \\ | & & | \\ CHO\text{-}OC\text{-}(CH_2)_7\text{-}CH=CH\text{-}(CH_2)_7\text{-}CH_3 + 3H_2 & = & CHO\text{-}OC\text{-}C_{17}H_{35} \\ | & & | \\ CH_2O\text{-}OC\text{-}(CH_2)_7\text{-}CH=CH\text{-}(CH_2)_7\text{-}CH_3 & & CH_2O\text{-}OC\text{-}C_{17}H_{35} \end{array}$$

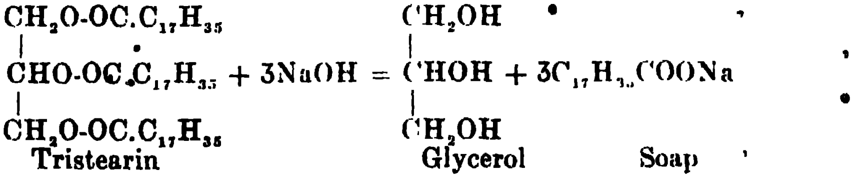
Triolein (liquid) Tristearin (solid)

Industrially, the liquid fatty oils, usually vegetable oils (which are rich in unsaturated glycerides), are treated with pure hydrogen under pressure at about 200° in presence of finely divided nickel catalyst. The unsaturated glycerides combine directly with hydrogen to give saturated glycerides. The result is solid fats. The nickel is removed by filter-pressing the hydrogenated (or hardened) oil. The process is known as *hydrogenation* or *hardening of oils*. Hydrogenated vegetable oils, mostly groundnut oil, called 'Vanaspati' in India, is produced in large amounts and is consumed mainly for cooking purposes.

Butter.—Butter fat (from cow's milk) consists mainly of stearin, palmitin and olein (about 90 per cent), with about 7 per cent tributyrin (glyceride of butyric acid). On keeping butter slowly becomes rancid due to liberation of free butyric acid by hydrolysis of butyrin. The rancid butter becomes unfit for use because of disagreeable smell of butyric acid. The butter may be renovated by washing it with sodium bicarbonate solution which removes the butyric acid or by blowing steam through molten butter which volatalises butyric acid.

Soap.—Soap is a sodium (or potassium) salt of higher fatty acids such as palmitic and stearic acids. Sodium salts give hard soaps, such as are used in toilet and washing soaps, whereas potassium salts make soft soaps and are used for the preparation of shaving soaps. Soap is soluble in water and the solution has cleansing properties.

Soap is made by saponification (alkaline hydrolysis) of fats and oils by boiling with caustic soda solution, when the sodium salt of the fatty acids, i.e., soap is formed and glycerol is set free :



$$\begin{array}{lcl} CH_2O\text{-}OC.C_{17}H_{35} & & CH_2OH \\ | & & | \\ CHO\text{-}OC.C_{17}H_{35} + 3NaOH & = & CHOH + 3C_{17}H_{35}COONa \\ | & & | \\ CH_2O\text{-}OC.C_{17}H_{35} & & CH_2OH \end{array}$$

Tristearin Glycerol Soap

A mixture of fats and oils, e.g., a mixture of tallow, groundnut oil and cocoanut oil, is boiled with a slight excess of caustic soda solution in a kettle which is heated by steam pipes until saponification is complete. Common salt is then added to precipitate the soap from the solution ('salting out'). Two layers separate—the top layer is soap and the bottom aqueous layer contains the glycerine, salt and unused alkali. The aqueous layer, known as *soap lye*, is drawn off and is used for the recovery of glycerine. The fluid mass of soap s then run off and allowed to solidify in slabs, and then cut into bars, and dried, and may be used as washing soaps. In order to make toilet soaps the bars are shredded into soap chips, which are dried and uniformly mixed with colour and perfumes and finally made into cakes.

In the *cold process* a mixture of tallow and cocoanut oil is saponified with strong caustic solution at ordinary temperature—the entire mass sets to a hard soap.

Transparent soap is made by dissolving soap in methylated spirit; after driving off the alcohol the liquid sets to a transparent mass on cooling.

Hydrolysis of fats and oils.—The hydrolysis of fats to produce fatty acids and glycerine is carried out by heating with water under pressure in presence of lime or magnesia. The fatty acids separate at the top and are removed, the aqueous bottom layer contains glycerine :

$$\text{Fats and oils} + H_2O \rightleftharpoons \text{glycerol} + \text{fatty acids.}$$

The fats also undergo similar hydrolysis in presence of Twitchell's reagent (complex organic acids) or the enzyme *lipase* present in castor seeds. Hydrolysis by heating with aqueous alkali produces salts of fatty acids (soap) and glycerol. The alkaline hydrolysis is known as *saponification*, i.e., soap making. But the term saponification is applied to hydrolysis of esters generally.

Stearic acid, made by splitting of fats, is used in making candles and face creams.

The fats and oils, also called '*fixed oils*' as they cannot be ordinarily distilled off, should be distinguished from : (i) *mineral oils* which are petroleum products, e.g., petrol, kerosene, etc., and (ii) *essentiol oils*, which are fragrant volatile constituents of certain plants, e.g., oil of turpentine, oil of wintergreen, oil of cinnamon, etc.

Waxes.—Waxes differ chemically from fats and oils in being **esters** of higher monohydric alcohols (of the methyl alcohol series) and higher fatty acids, e.g., *bees wax* consists chiefly of palmitate of myricyl alcohol ($C_{30}H_{61}.OH$) and *Spermaceti* (found in the head of sperm whale) is mainly palmitate of cetyl alcohol ($C_{16}H_{33}.OH$).

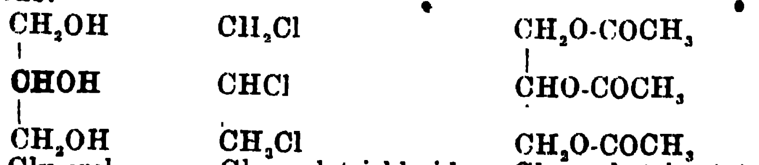
Glycerol, glycerine, $C_3H_5(OH)_3$, is the common constituent of all fats and oils (p. 56) which are the main source for its preparation.

Fats and oils on hydrolysis give glycerol and fatty acids (p. 58). After the separation of the fatty acids or their salts, the aqueous liquor is worked for glycerol. The soap lye (p. 57) which contains 5-8 per cent glycerol, common salt and free alkali, is the chief source of glycerol. The soap lye is *acidified*, and filtered from the insoluble fatty and resinous matters, and then neutralised and concentrated *under reduced pressure* in vacuum evaporators to a thick syrup—the salt crystallises out in course of evaporation and is removed. The crude glycerol is purified by distillation under reduced pressure in a current of steam. The distillate which contains pure glycerine and also some water, is evaporated in a vacuum pan to remove the water, and pure glycerine is obtained.

A small amount (about 3 per cent) of glycerol is present in the products of alcoholic fermentation (p. 26). But the yield of glycerol may be made as high as 30%, if fermentation is carried out in presence of sodium sulphite. Germany made glycerol by this process during the first global war, when she was short of fats.

Propylene from cracked petroleum is used in making synthetic glycerol.

Properties.—Glycerol is a colourless, viscous liquid (sp. gr. 1·26 at 15°) having a distinctly sweet taste. It boils at 290° with slight decomposition, and hence it is distilled under reduced pressure or in a current of steam. It is very hygroscopic and is soluble in water and alcohol, but not in ether. It is a trihydric alcohol, and exhibits the chemical properties of alcohol, but in a threefold degree. Thus, it forms glycerol trichloride with PCl_5, and glyceryl triacetate with acetic anhydride.



$$\begin{array}{lll} CH_2OH & CH_2Cl & CH_2O\text{-}COCH_3 \\ | & | & | \\ CHOH & CHCl & CHO\text{-}COCH_3 \\ | & | & | \\ CH_2OH & CH_2Cl & CH_2O\text{-}COCH_3 \end{array}$$

Glycerol Glycerol trichloride Glyceryl triacetate

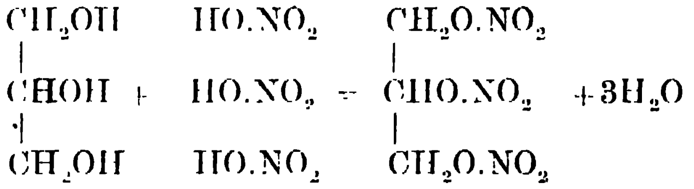
Tests.—(i) **Acrolein test:** On heating with powdered potassium bisulphate, glycerol evolves acrolein, $CH_2{=}CH\text{-}CHO$, having a pungent and irritating smell.

$$CH_2OH\text{-}CHOH\text{-}CH_2OH \longrightarrow CH_2{=}CH.CHO + 2H_2O$$

(ii) **Borax-phenolphthalein test**—The pink colour that develops on adding phenolphthalein to an aqueous solution of borax, disappears on adding glycerol. But the colour reappears on heating.

Uses.—Glycerol is mainly used in making nitroglycerine, and hence explossives. But glycerol has other uses also, e.g., in the preparation of plastics, toilet soaps, cosmetics, copying ink, water-colour pigments, shoe polish, etc.; as an anti-freeze in motor car radiators; in gas meters to avoid evaporation (in summer) and freezing (in winter); to preserve fruits and tobacco; and also in medicine.

Nitroglycerine. Nobel's oil, $C_3H_5.(ONO_2)_3$, is made by slowly adding pure glycerol to a well-cooled mixture of concentrated sulphuric acid and fuming nitric acid. The temperature must not rise above 30°. The mixture is allowed to stand, when nitroglycerine forms a layer on the surface. It is run into water, where it separates as a heavy oil. It is washed with water and then sodium carbonate solution to remove all traces of acid and finally dried over anhydrous sodium carbonate. *Being highly explosive, it is an extremely dangerous substance, and its preparation is safe only to expert chemists.*

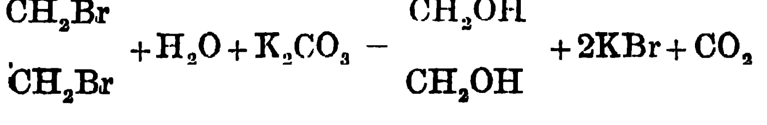


$$\begin{array}{llllll} CH_2OH & & HO.NO_2 & & CH_2O.NO_2 & \\ | & & & & | & \\ CHOH & + & HO.NO_2 & = & CHO.NO_2 & +3H_2O \\ | & & & & | & \\ CH_2OH & & HO.NO_2 & & CH_2O.NO_2 & \end{array}$$

Nitroglycerine is really an ester of nitric acid, namely, glyceryl trinitrate, but is incorrectly called nitroglycerine.

It is a heavy colourless liquid. It explodes violently when suddenly heated, or struck or detonated. Nitroglycerine alone is unsuited for use as an explosive, as it is likely to explode under mechanical shock. Mixed with kieselguhr (a porous siliceous earth which absorbs nitroglycerine) it forms *dynamite*, which it is safe to handle and transport. Nitroglycerine is used in making *cordite* (smokeless gunpowder') which is a mixture of nitroglycerine (30%), guncotton (65%) and vaseline (5%). Nitroglycerine is used in medicine in cases of heart disease.

Glycol, ethylene glycol, $CH_2OH.CH_2OH$, is a dihydric alcohol, and is made in the laboratory by hydrolysis of ethylene dibromide by boiling with K_2CO_3 solution. The glycol is separated by distillation.



$$\begin{array}{lll} CH_2Br & & CH_2OH \\ & +H_2O+K_2CO_3 = & \qquad +2KBr+CO_2 \\ CH_2Br & & CH_2OH \end{array}$$

Ethylene is oxidised to glycol by cold dilute alkaline potassium permanganate solution (p. 13).

$$CH_2=CH_2+H_2O+O = CH_2OH.CH_2OH$$

Glycol is made commercially by hydrolysis of ethylene chlorohydrin by sodium bicarbonate solution. Ethylene chlorohydrin is first made by the action of hypochlorous acid upon ethylene (obtained from cracked petroleum).

$$CH_2=CH_2 + HOCl = CH_2Cl.CH_2OH \text{ (ethylene chlorohydrin)}$$

$$CH_2Cl.CH_2OH + NaHCO_3 = CH_2OH.CH_2OH + NaCl + CO_2$$

Properties.—Glycol is a colourless, viscid liquid (b.p. 197° ; sp. gr. 1·125) with a sweet taste, (and hence the name: Greek *glukus*, sweet). It is hygroscopic and is soluble in alcohol and water, but very sparingly in ether (*cf.* glycerine).

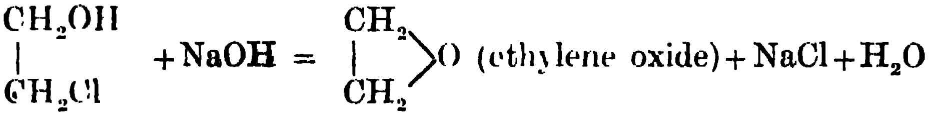
Glycol contain two primary alcoholic groups and exhibits alcoholic properties in a twofold degree. Metallic sodium gives mono- and di-sodium glycollate, with liberation of hydrogen, e.g., $CH_2OH.CH_2ONa$ and $CH_2ONa.CH_2ONa$. Acetyl chloride similarly gives glycol mono- and di-acetate, e.g., $CH_2OH.CH_2O.COCH_3$ and $CH_2.(O.COCH_3)$. $CH_2.(O.COCH_3)$. PCl_5 gives ethylene dichloride, $CH_2Cl.CH_2Cl$.

$$CH_2OH.CH_2OH+2PCl_5 = CH_2Cl\text{-}CH_2Cl+2POCl_3+2HCl$$

But HCl replaces only one hydroxyl, giving ethylene chlorohydrin, $CH_2OH.CH_2Cl$.

$$CH_2OH.CH_2OH+HCl = CH_2OH.CH_2Cl+H_2O.$$

On heating with strong caustic soda ethylene chlorohydrin gives ethylene oxide.



$$\begin{array}{l}CH_2OH\\ |\\ CH_2Cl\end{array} + NaOH = \begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>O \text{ (ethylene oxide)} + NaCl + H_2O$$

Glycol, a di-primary alcohol, can give various products by successive oxidation of the CH_2OH groups into -CHO and then -COOH groups, e.g.

CH_2OH	CH_2OH	CHO	CHO	$COOH$
CHO .	$COOH$	CHO	$COOH$	$COOH$
Glycollic aldehyde	Glycollic acid	Glyoxal	Glyoxalic acid	Oxalic acid

As glycol freezes at −11·5°, it is used as an anti-freeze in motor car radiators. It is used as a cooling liquid in aeroplane engine, and for de-icing aeroplane. It is also used as a solvent.

XI

AMINES

The amines.—The amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by alkyl groups, such as methyl, $-CH_3$, ethyl, $-C_2H_5$, etc. There are *three* types of amines, as illustrated by three methylamines.

CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
Methylamine	**Dimethyamine**	**Trimethylamine**
(Primary amine)	**(Secondary amine)**	**(Tertiary amine)**

They are called primary, secondary and tertiary amines, according as one, two or three hydrogen atoms of ammonia are replaced by alkyl groups. A primary amine contains the *amino group*, $-NH_2$, a secondary amine the *imino* group, $=NH$, and a tertiary amine the *nitrile* group, $\equiv N$, in the molecule.

Preparation of amines.—The amines may be prepared by:

(i) **Alkylation of ammonia** by heating an alkyl halide, such as methyl iodide, CH_3I, with alcoholic ammonia (alcohol saturated with ammonia) in a sealed tube (Hofmann's method). Three classes of amines as well as a tetra alkyl ammonium salt are formed together in the reaction.

$$NH_3 + CH_3I = CH_3NH_2 + HI$$
$$CH_3NH_2 + CH_3I = (CH_3)_2NH + HI$$
$$(CH_3)_2NH + CH_3I = (CH_3)_3N + HI$$
$$(CH_3)_3N + CH_3I = (CH_3)_4NI \text{ (Tetramethyl ammonium iodide.)}$$

The alkylation of ammonia may also be carried out by passing a mixture of alcohol vapour and ammonia over heated thoria (Sabetier's method).

$$CH_3OH + NH_3 = CH_3NH_2 + H_2O$$

(ii) **Reduction of nitroparaffins** with tin and hydrochloric acid (or sodium and alcohol) gives primary amines.

$$CH_3NO_2 + 3H_2 = CH_3NH_2 + 2H_2O$$

(iii) **Reduction of alkyl cyanide** gives a primary amine (Mendius reaction). Reduction is done by sodium and alcohol or by hydrogen in presence of heated nickel: $CH_3CN + 2H_2 = CH_3CH_2NH_2$.

Oximes on similar reduction give primary amines.

$$CH_3CH = NOH + 2H_2 = CH_3CH_2NH_2 + H_2O$$

(iv) Hydrolysis of alkyl isocyanate by boiling aqueous alkali gives a primary amine (Wurtz's method).

$$CH_3\text{-}N = C = O \text{ (methyl isocyanate)} + 2KOH = CH_3NH_2 + K_2CO_3$$

(v) **Hofmann's reaction** offers the readiest method to prepare a primary amine from the amide of a fatty acid. The method consists in heating the acid amide with an alkaline solution of sodium hypochlorite or hypobromite. An atom of carbon is eliminated from the amide and a primary amine results.

$$CH_3CONH_2 + NaOBr = CH_3NH_2 + CO_2 + NaBr$$

Acetamide first forms acetobromamide, $CH_3CONHBr$. The acetobromamide then splits off HBr and methyl isocyanate, CH_3NCO, is formed by atomic rearrangement. The methyl isocyanate is hydrolysed by alkali, giving methylamine.

$$CH_3CONH_2 + NaOBr = CH_3CONHBr + NaOH$$
$$CH_3CONHBr + NaOH = CH_3NCO + NaBr + H_2O$$
$$CHNCO + 2NaOH = CH_3NH_2 + Na_2CO_3$$

The reaction may also be carried out, using bromine and caustic alkali, as follows: Dilute aqueous caustic potash (10%) is slowly added to a cold solution of equal weights of acetamide and bromine until the colour of bromine disappears. Acetobromamide results.

$$CH_3CONH_2 + Br_2 = CH_3CONHBr + HBr$$

The solution is then heated with a concentrated solution of potash, when a strong ammoniacal but slightly fishy smell of methylamine is noticed.

Propionamide, $CH_3CH_2CONH_2$, similarly gives ethylamine, $CH_3CH_2NH_2$.

$$CH_3CH_2CONH_2+NaOBr = CH_3CH_2NH_2+CO_2+NaBr$$

(vi) A direct reaction of a fatty acid with hydrazine, N_3H, gives primary amine in excellent yield. $CH_3COOH + N_3H = CH_3NH_2 + CO_2 + N_2$.

Methylamine may be obtained by heating ammonium chloride with excess of formaldehyde at 130°. $2NH_4Cl + 3HCHO = 2CH_3NH_2.HCl + H_2O + CO_2$

Properties of amines.—(i) The lower members, such as methyl amine, CH_3NH_2, and ethyl amine, $C_2H_5NH_2$, are inflammable gases, which are readily soluble in water. They have a strong fishy-ammoniacal smell.

(ii) The amines are *monoacid organic bases*. They are stronger bases than ammonia. Their aqueous solutions turn red litmus blue.

$$CH_3NH_2 + H_2O \rightleftharpoons (CH_3NH_3)OH \rightleftharpoons (CH_3NH_3)^+ + OH^-$$

$$(cf.\ NH_3 + H_2O \rightleftharpoons (NH_4)OH \rightleftharpoons NH_4^+ + OH^-)$$

Like ammonia, the amines form crystalline salts with mineral acids, which are readily soluble in water, e.g., methylamine hydrochloride, $(CH_3NH_3)Cl$, methylamine sulphate, $(CH_3NH_3)_2SO_4$. They form salts with chloroplatinic acid, H_2PtCl_6, e.g., methylamine chloroplatinate, $(CH_3NH_3)_2.PtCl_6$, (*cf.* ammonium chloroplatinate, $(NH_4)_2.PtCl_6$). The chloroplatinnates are used in determining the molecular weight of amines.

(iii) **Action of nitrous acid.**—A primary amine reacts with nitrous acid, giving alcohol, nitrogen and water.

$$\begin{matrix}CH_3\text{-}NH_2\\ HONO\end{matrix} = CH_3OH+N_2+H_2O$$

Nitrous acid acts on a secondary amine, giving a yellow oil, called *nitrosoamine*. $(CH_3)_2NH+HONO = (CH_3)_2N.NO+H_2O$
Dimethyl nitrosoamine

Nitrous acid is without action upon a tertiary amine. Nitrous acid, therefore, serves to distinguish between three types of amines.

(iv) **Acetylation.**—Acetyl chloride (or acetic anhydride) acts on primary and secondary amines to give amides, but is without action on a tertiary amine.

$CH_3NH_2+ClCOCH_3 = CH_3NH.COCH_3$ (methyl acetamide) + HCl.
$(CH_3)_2NH+ClCOCH_3 = (CH_3)_2N.COCH_3$ (dimethyl acetamide) + HCl.

(v) **Carbylamine reaction.**—When a primary amine is warmed with chloroform and alcoholic potash, a carbylamine or isocyanide having intolerable smell is formed. (p. 22).

$$CH_3NH_2+CHCl_3+3KOH = CH_3NC+3KCl+3H_2O$$
Methyl isocyanide

Secondary and tertiary amines do not give carbylamine reaction.

(vi) **Methylation.**—A tertiary amine reacts with only *one molecule* of methyl iodide at ordinary pressure to give what are known as *quaternary ammonium iodides.* Trimethylamine, $(CH_3)_3N$, gives the quaternary ammonium salt, tetramethyl ammonium iodide, $N(CH_3)_4I$.

$$(CH_3)_3N + CH_3I = N(CH_3)_4I$$

The quaternary ammonium salt is undecomposed by hot caustic alkali, but reacts with moist silver oxide, giving quaternary ammonium hydroxide. $N(CH_3)_4I + AgOH = N(CH_3)_4OH + AgI$

The tetramethyl ammonium hydroxide, $N(CH_3)_4OH$, is a strong base, and gives tri-methyl amine on heating:

$$N(CH_3)_4OH = N(CH_3)_3 + CH_3OH$$

Primary and secondary amines, however, on heating with methyl iodide under pressure in a sealed tube, give tertiary amines and finally quaternary ammonium iodides.

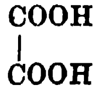
Test for amides and amines.—The reactions stated above serve to distinguish between primary, secondary and tertiary amines.

An amide on alkaline hydrolysis evolves ammonia (p. 51), but a primary amine, e.g., CH_3NH_2, is not hydrolysed with acid or alkali. Both amide and primary amine react with nitrous acid, evolving nitrogen, but the amide gives an acid (p. 51) and an amine an alcohol (p. 62). Amines readily form salts with aqueous solutions of acids, but amides do not.

XII

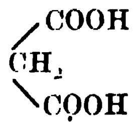
DIBASIC ACIDS

The dicarboxylic acids contain two -COOH groups and hence two replaceable hydrogen atoms ; they are therefore, dibasic acids. The

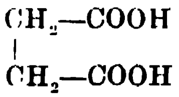


$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

Oxalic acid



Malonic acid



$$\begin{array}{l} CH_2—COOH \\ | \\ CH_2—COOH \end{array}$$

Succinic acid

and so on.

Oxalic acid, HOOC-COOH.—Wood sorrel and other plants contain potassium hydrogen oxalate, sometimes called *salts of sorrel.* Calcium oxalate crystals are found in certain plant cells.

Preparation.—(i) In the laboratory oxalic acid is made by gently heating cane sugar with concentrated nitric acid.

$$C_{12}H_{22}O_{11} + 9O_2 = 6(COOH)_2 + 5H_2O$$

Strong nitric acid (200 c.c.) is taken in a large flask and heated on water bath. The flask is removed to a fume cupboard and 50 gms. of cane sugar added. Torrents of brown fumes are evolved. After the reaction has ceased, the solution is concentrated in a basin on a water bath. Large crystals of oxalic acid separate on cooling.

(ii) Commercially, oxalic acid is made from: (a) Pine sawdust by heating (avoiding charring) with caustic soda in iron pans to about 250°—fused alkali oxidises cellulose (in the sawdust) into sodium oxalate. The fused mass is extracted with water. The solution contains sodium oxalate, which on boiling with milk of lime precipitates calcium oxalate. The calcium oxalate is separated and decomposed by calculated amount of dilute H_2SO_4.

$$Ca(COO)_2 + H_2SO_4 = CaSO_4 + (COOH)_2$$

The $CaSO_4$ is filtered off. The filtrate on concentration and cooling, gives crystals of oxalic acid.

(b) Sodium formate (p. 44) by heating to 350°-400° when sodium oxalate is formed. Oxalic acid is made from the sodium oxalate in the same way as in (a) above. $2H.COONa = H_2 + (COONa)_2$

Properties. —(i) Oxalic acid crystallises from water in colourless, hydrated prisms, $(COOH)_2, 2H_2O$. The crystals of dihydrate lose water of crystallisation at 100° and become anhydrous. But at higher temperatures it decomposes into formic acid and carbon dioxide.

$$HOOC\text{-}COOH = H.COOH + CO_2$$

It is soluble in water and alcohol, but only sparingly in ether.

(ii) Heating with conc. H_2SO_4 decomposes oxalic acid, evolving CO and CO_2. $HOOC\text{-}COOH = H_2O + CO_2 + CO$.

(iii) It is a dibasic acid and forms normal salts, e.g., potassium oxalate, $K_2C_2O_4$, soluble in water, and acid salts e.g., potassium hydrogen oxalate, KHC_2O_4, which is less soluble.

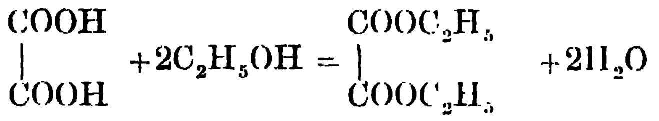
(iv) Oxalic acid rapidly decolorises potassium permanganate solution in presence of dilute sulphuric acid, on warming, and is thereby oxidised to CO_2 and water. The reaction is used in volumetric analysis.

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

(v) Reaction with PCl_5 gives oxalyl chloride, $(COCl)_2$, b.p. 64°

$$HOOC\text{-}COOH + 2PCl_5 = ClOC\text{-}COCl + 2POCl_3 + 2HCl$$

(vi) Esters are made by distilling oxalic acid with alcohol. Ethyl alcohol gives ethyl oxalate, a liquid, b.p. 186°.



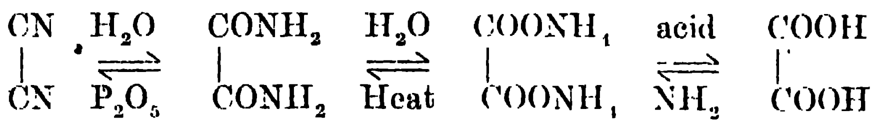
$$\begin{matrix}COOH\\|\\COOH\end{matrix} + 2C_2H_5OH = \begin{matrix}COOC_2H_5\\|\\COOC_2H_5\end{matrix} + 2H_2O$$

Methyl oxalate is a solid, m.p. 51°.

(vii) Ammonium oxalate on heating gives oxamide, $(CONH_2)_2$.

$$H_4NOOC\text{-}COONH_4 = H_2NOC\text{-}CONH_2 + 2H_2O$$

(viii) On heating with P_2O_5, oxamide gives off cyanogen, $(CN)_2$, a poisonous gas. Cyanogen is the nitrile of oxalic acid, as it yields oxamide and finally oxalic acid on acid hydrolysis.



$$\begin{matrix}CN\\|\\CN\end{matrix} \underset{P_2O_5}{\overset{H_2O}{\rightleftharpoons}} \begin{matrix}CONH_2\\|\\CONH_2\end{matrix} \underset{Heat}{\overset{H_2O}{\rightleftharpoons}} \begin{matrix}COONH_4\\|\\COONH_4\end{matrix} \underset{NH_3}{\overset{acid}{\rightleftharpoons}} \begin{matrix}COOH\\|\\COOH\end{matrix}$$

(ix) A neutral solution of an oxalate gives a white precipitate of calcium oxalate with $CaCl_2$ solution ; the precipitate is insoluble in acetic acid. Reactions (ii), (iv) and (ix) are used as *tests* for oxalic acid.

Oxalic acid and its salts are poisonous.

Uses of oxalic acid.—Oxalic acid is used in printing and dyeing, in making inks and metal polish, in removing ink stains, and for bleaching straws for hats. *Potassium quadro oxalate*, $KHC_2O_4.H_2C_2O_4.2H_2O$, also known as *salts of sorrel, or lemon*, is used to remove ink stains and ink moulds. *Potassium ferrous oxalate*, $K_2Fe(C_2O_4)_2.H_2O$, is a photographic developer.

Malonic acid, HOOC-CH$_2$-COOH, occurs as calcium salt in beet root. It is synthesised from monochloro-acetic acid (p. 47). On boiling with KCN, potassium chloroacetate gives potassium cyanacetate, which on hydrolysis with boiling HCl gives malonic acid. It is a solid, m.p. 132°.

$$CH_2Cl.COOK + KCN = CH_2(CN).COOK + KCl$$

$$CH_2(CN).COOK + 2H_2O + 2HCl = CH_2.(COOH)_2 + NH_4Cl + KCl$$

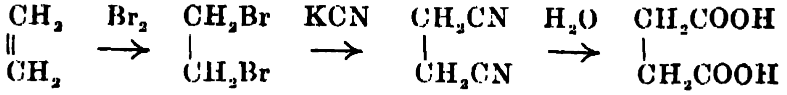
Malonic acid loses carbon dioxide on heating :

$$HOOC\text{-}CH_2\text{-}COOH = CH_3.COOH + CO_2$$

This illustrates that a polybasic acid having two -COOH groups linked to the same carbon atom, loses CO$_2$ on heating.

Malonic ester, diethyl malonate, CH$_2$.(COOC$_2$H$_5$)$_2$, oily liquid, b.p. 198°, is well-known for its synthetic uses.

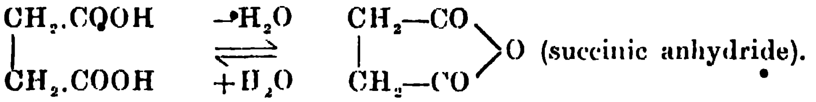
Succinic acid, HOOC-CH$_2$-CH$_2$-COOH, is present in lignite (fossil wood) and in many plants. It was first obtained by distillation of amber (Latin, *succinum*) and hence the name. It may be synthesised from ethylene in the following way :



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \xrightarrow{Br_2} \begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} \xrightarrow{KCN} \begin{matrix} CH_2CN \\ | \\ CH_2CN \end{matrix} \xrightarrow{H_2O} \begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix}$$

Ethylene can be obtained by dehydrating ethyl alcohol (p. 29).

Succinic acid is a crystalline solid, m.p. 185°, sparingly soluble in cold water, alcohol and ether. On heating it gives succinic anhydride, which is converted into the acid on hydrolysis with boiling water.



$$\begin{matrix} CH_2.COOH \\ | \\ CH_2.COOH \end{matrix} \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} \begin{matrix} CH_2\text{—}CO \\ | \\ CH_2\text{—}CO \end{matrix}\!\!>O$$

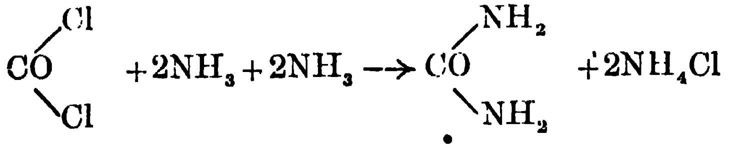
(succinic anhydride).

Succinic acid is used for standardisation of alkalis.

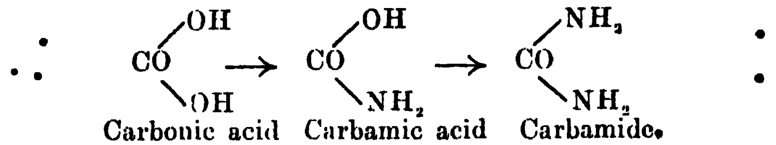
Urea, carbamide, H$_2$N-CO-NH$_2$, is found in the urine of mammals and of carnivorous birds and reptiles. It occurs in human urine—an adult passes out 30 gms. of urea daily.

Being one of the final decomposition products of waste nitrogeneous material of the body, urea is a compound of great physiological interest.

Carbonyl chloride, COCl$_2$, reacts with ammonia, giving urea. The reaction shows that *urea is a diamide of carbonic acid.*



$$CO\begin{matrix} Cl \\ Cl \end{matrix} + 2NH_3 + 2NH_3 \longrightarrow CO\begin{matrix} NH_2 \\ NH_2 \end{matrix} + 2NH_4Cl$$



$$CO\begin{matrix} OH \\ OH \end{matrix} \longrightarrow CO\begin{matrix} OH \\ NH_2 \end{matrix} \longrightarrow CO\begin{matrix} NH_2 \\ NH_2 \end{matrix}$$

Carbonic acid Carbamic acid Carbamide.

Preparation.—(i) Urea may be isolated from human urine by evaporating to a residue on a waterbath, and then extracting the residue with alcohol which dissolves urea. The alcoholic solution on evaporation gives urea.

(ii) The synthesis of urea from ammonium cyanate by Wohler in 1828 is of historical importance (p. 1), it being the first organic compound to be prepared artificially.

An aqueous solution of ammonium cyanate (or a mixture of potassium cyanate and ammonium sulphate in equimolecular amounts) on evaporation to

UTTARPARA

dryness on a water bath gives urea. The residue is extracted with alcohol which dissolves urea. The alcoholic solution yields urea on evaporation.

$$NH_4CNO = NH_2\text{-}CO\text{-}NH_2$$

Ammonium cyanate changes into urea by atomic rearrangement. Ammonium cyanate and urea are *isomeric* with one another.

Urea is made *commercially* by heating to 130°-140° a mixture of ammonia and carbon dioxide under a presseure of 150-200 atmospheres. Ammonium carbamate first formed decomposes into urea and water.

$$2NH_3 + CO_2 = H_2N\text{-}CO\text{-}ONH_4 \text{ (ammonium carbamate)}$$

$$H_2N\text{-}CO\text{-}ONH_4 = CO(NH_2)_2 + H_2O$$

Properties.—(i) Urea is a colourless crystalline solid (m.p. 132°) *and is readily soluble in water and alcohol, but is insoluble in ether.*

(ii) *It is a monoacid base*—the aqueous solution is, however, neutral to litmus. On adding (a) concentrated HNO_3, (b) concentrated oxalic acid solution, to a concentrated solution of urea, crystalline precipitate of urea nitrate, $CO(NH_2)_2$, HNO_3, and urea oxalate, $CO(NH_2)_2$, $H_2C_2O_4$, are formed.

(iii) **Biuret reaction.**—On *gentle* heating urea melts and evolves ammonia, forming a substance, called *biuret*. Two molecules of urea interact with elimination of ammonia, forming biuret.

$$H_2N\text{-}CO\text{-}NH_2 + H_2N\text{-}CO\text{-}NH_2 = H_2N\text{-}CO\text{-}NH\text{-}CO\text{-}NH_2 + NH_3$$

On heating for a minute or two after the evolution of ammonia, a solid mass appears. This is cooled and dissolved in a few drops of water. On adding a drop or two of *dilute* copper sulphate solution and finally caustic soda solution, a *pink* or *violet* colour develops. This is a delicate test for urea.

(iv) Nitrous acid (mixture of $NaNO_2$ and HCl) decomposes urea, giving off $CO_2$and N_2.

$$\begin{array}{l} H_2N\text{—}CO\text{—}NH_2 \\ ONOH \quad HONO \end{array} = 2N_2 + CO_2 + 3H_2O$$

(v) Alkaline solution of sodium hypochlorite, NaOCl, or sodium hypobromite, NaOBr, also reacts, giving off CO_2 and N_2.

$$\begin{array}{l} \quad H_2N\text{- -}CO\text{—}NH_2 = N_2 + CO_2 + 2H_2O + 3NaBr \\ NaOBr \; NaOBr \; NaOBr \end{array}$$

The nitrogen may be collected over alkali (to absorb CO_2) in Lunge's nitrometer; its volume gives a rough measure of urea in a solution. Urea in urine may be roughly estimated in this way.

(vi) **Hydrolysis.**—Like other amides, it is hydrolysed by boiling caustic alkali or acids. Boiling with alkali evolves ammonia.

$$H_2N\text{-}CO\text{-}NH_2 + 2NaOH = Na_2CO_3 + 2NH_3$$

At ordinary temperature the enzyme *urease* (present in soybeans) hydrolyses urea into ammonium carbonate (ammonia and CO_2). Ammonia is liberated by adding K_2CO_3 and distilled into standard acid and estimated. The ammonia formed gives an estimate of urea in the solution. $CO(NH_2)_2+H_2O = 2NH_3+CO_2$

Uses.—Urea is used : (i) as a fertilizer in agriculture, (ii) in making synthetic plastics (urea-formaldehyde resins) and various drugs, e.g., veronal, urea-stibamine.

XIII

HYDROXY ACIDS

The hydroxy acids are compounds which combine the properties of alcohols and acids, i.e., they contain both hydroxyl and carboxyl groups, e.g., hydroxy acetic acid (glycollic acid), $CH_2(OH).COOH$.

Glycollic acid, $CH_2(OH).COOH$, occurs in unripe grapes. It is a colourless, crystalline solid, m.p. 80°, soluble in water, alcohol and ether.

It is made : (i) by hydrolysis of potassium chloroacetate with boiling water, when the chlorine atom is replaced by an OH- group, yielding glycollic acid.

$$CH_2Cl.COOK + H.OH - CH_2(OH)COOH + KCl$$

(ii) by careful oxidation of glycol by hot dilute HNO_3.

$$HOH_2C\text{-}CH_2OH + O_2 = CH_2(OH).COOH + H_2O$$

(iii) by hydrolysis of formaldehyde cyanhydrin.

$$CH_2(OH).CN + 2H_2O = CH_2(OH)COOH + NH_3$$

It contains a primary alcoholic group, $-CH_2OH$, and a $-COOH$ group, and therefore, gives the properties of both. Thus :

(i) It forms salt with alkali, e.g., sodium glycollate, $CH_2OH.COONa$, and ester with alcohol, e.g., ethyl glycollate, $CH_2OH.COOC_2H_5$.

The ethyl glocollate reacts with acetyl chloride—the H atom of the hydroxyl being replaced by the acetyl group $-COCH_3$.

$$CH_2(OH).COOC_2H_5 + ClCOCH_3 = CH_2(OCOCH_3).COOC_2H_5 + HCl$$

(ii) Metallic sodium replaces hydrogen of both hydroxyl and carboxyl groups, giving disodium glycollate, $CH_2(ONa).COONa$. PCl_5 replaces both the OH groups by chlorine, giving chloroacetyl chloride, $CH_2Cl.COCl$.

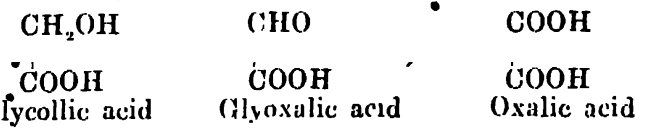
(iii) It is reduced to acetic acid by hydriodic acid.

$$CH_2(OH).COOH + 2HI = CH_3\text{-}COOH + H_2O + I_2$$

But hydrobromic acid, HBr, gives bromoacetic acid.

$$CH_2(OH).COOH + HBr = CH_2Br.COOH + H_2O$$

(iv) On oxidation, it first gives glyoxalic acid, and finally oxalic acid.



$$\begin{array}{ccc} CH_2OH & CHO & COOH \\ | & | & | \\ COOH & COOH & COOH \end{array}$$

Glycollic acid Glyoxalic acid Oxalic acid

Lactic acid, α-hydroxy propionic acid, $CH_3.CHOH.COOH$, occurs in sour milk from which it was first isolated by Scheele in 1870, and hence the name. It is formed in milk by fermentation of milk sugar (lactose, $C_{12}H_{22}O_{11}$) by *bacillus aceti lacti.*

$$C_{12}H_{22}O_{11}+H_2O = 4CH_3CH(OH).COOH.$$

Commercially, lactic acid is made by adding sour milk or decayed cheese (which supplies the ferment *Bacillus aceti lacti*) into a solution of cane sugar or starch in presence of calcium or zinc carbonate. During fermentation extending over several days, the temperature is kept at 35-40°. The lactic acid formed is neutralised by the calcium or zinc carbonate, giving crystals of calcium (or zinc) lactate. These are decomposed with dilute sulphuric acid, and the lactic acid is extracted with ether. The lactic acid is obtained as a viscid liquid on evaporating the ether.

Lactic acid may be synthesised: (i) by hydrolysis of α-chloro (or bromo) propionic acid by boiling with water (the carbon atom next to the carboxyl group is called the α-carbon atom).

$$CH_3.CHCl.COOH + H.OH \quad CH_3.CHOH.COOH + HCl$$

Propionic acid on chlorination or bromination in presence of red P or I, gives α-chloro (or bromo) propionic acid.

$$CH_3CH_2COOH + Cl_2 \quad CH_3CHClCOOH + HCl$$

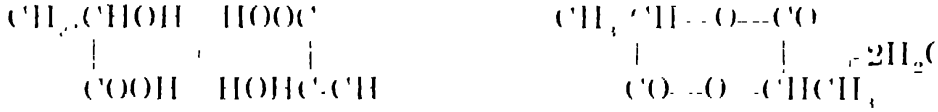
(ii) by hydrolysis of acetaldehyde cyanhydrin (p. 36).

$$CH_3CH(OH)CN + 2H_2O \quad CH_3CH(OH)COOH + NH_3$$

Properties. (i) Lactic acid is a colourless viscid liquid with a sour taste (m.p. 18°). It is highly hygroscopic, and is soluble in water, alcohol and ether.

(ii) It cannot be distilled unchanged at ordinary pressure, as it decomposes into CH_3CHO, CO and water; but it distils unchanged at 1 mm. pressure. $CH_3CH(OH)COOH \quad CH_3CHO + H_2O + CO$

(iii) It forms a *lactide* (a cyclic diester) on heating by elimination of two molecules of water.



(iv) It decomposes into CH_3CHO and $HCOOH$ on heating with dilute H_2SO_4. With conc. H_2SO_4, CO is evolved.

$$CH_3CH(OH)COOH \quad CH_3CHO + HCOOH$$

(v) It is a monobasic acid and forms salts and esters as usual, e.g., ethyl lactate, $CH_3CH(OH)COOC_2H_5$.

But the acid also contains a secondary alcoholic group CHOH, and behaves as such. On oxidation with hydrogen peroxide in presence of ferrous sulphate (Fenton's reagent), it gives pyruvic acid. $CH_3.CO.COOH$. $CH_3.CHOH.COOH + O = CH_3.CO.COOH + H_2O$

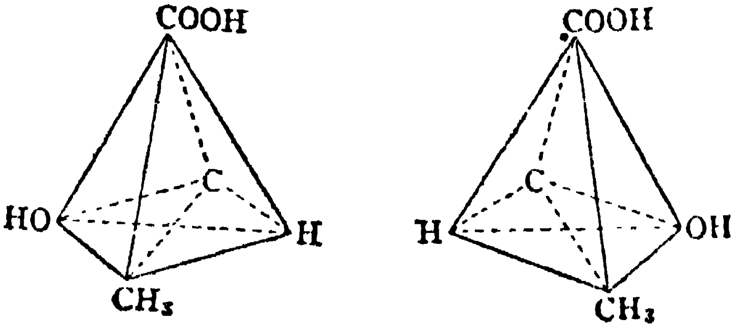
Lactic acid also gives iodoform reaction.

Uses.—Lactic acid and its salts are used in dyeing, tanning and calico-printing. Ethyl lactate is a solvent for lacquer varnish. Calcium lactate is used medicinally for calcium deficiency.

Optical isomerism of lactic acid.—Lactic acid exists in three isomeric forms. All the forms have the same structure and chemical composition and hence the same chemical properties, but they differ in physical properties and in their action on plane polarised light. Such compounds are called **optical isomers** or **stereo-isomers,** and the phenomenon is known as **optical isomerism** or **stereo-isomerism.**

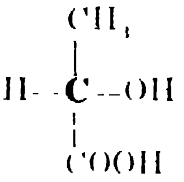
The phenomenon was clearly explained by Le Bel and van't Hoff in 1874. In order to explain optical isomerism it was necessary to represent quadrivalent carbon in three dimensions. The optical isomerism was interpreted in terms of the *arrangement in space* of different atoms or groups linked to the carbon atom.

It was assumed that the carbon atom is situated at the centre of an imaginary regular tetrahedron, and that its four valencies are directed in space in straight lines, drawn from the centre of the tetrahedron towards its four corners, as shown by the dotted lines (fig. 5). The angle between each pair of valency bonds is 109·5° and one pair lies in a plane at right angle to the plane of the other pair. Therefore, the valence bonds of a carbon atom are not distributed in one plane. All the four valencies are equally distributed in space.

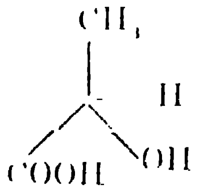


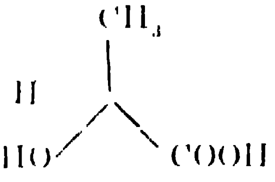
(i) Fig. 5 (ii)

Now, the space formula of a carbon atom attached to four different atoms or groups, can exist in two, but only two, different forms and they are related as an object to its mirror-image. Both the structures are asymmetric, i.e., they have no plane of symmetry. Lactic acid can exist in two such asymmetric forms, since it contains in its molecule an **asymmetric carbon** atom (shown in heavy type), i.e., *a carbon atom linked to four different atoms or groups*. The two isomeric forms of lactic acid are shown below:



$$\begin{array}{c} CH_3 \\ | \\ H-\mathbf{C}-OH \\ | \\ COOH \end{array}$$





Le Bel and van't Hoff attributed the optical activity of a compound to the presence of asymmetric carbon atoms in the molecule. Lactic acid exhibits optical activity due to the presence of an asymmetric carbon atom in the molecule. The asymmetry in the molecule is accompanied by optical activity.

Both forms of lactic acid (fig. 5) related as an object to its mirror image, are optically active, but their rotations, though equal in magnitude, are opposite in sign. One form turns the plane of polarised light to the right. This is called **dextro** or **d-lactic acid.** The **sarco-lactic acid** which is found in muscles, is d-lactic acid. The other form which turns the plane of polarised light to the left, is called **laevo** or **l-lactic acid.**

Equimolecular mixture of d- and l- lactic acids is optically inactive, since the dextro-rotation of the d-acid is neutralised by the lactate. These are decomposed with dilute sulphuric acid, and the lactic acid is extracted with ether. The lactic acid is obtained as a viscid liquid on evaporating the ether.

Lactic acid may be synthesised: (i) by hydrolysis of α-chloro (or bromo) propionic acid by boiling with water (the carbon atom next to the carboxyl group is called the α-carbon atom).

$$CH_3.CHCl.COOH + H.OH = CH_3.CHOH.COOH + HCl$$

Propionic acid on chlorination or bromination in presence of red P or I, gives α-chloro (or bromo) propionic acid.

$$CH_3CH_2COOH + Cl_2 = CH_3CHClCOOH + HCl$$

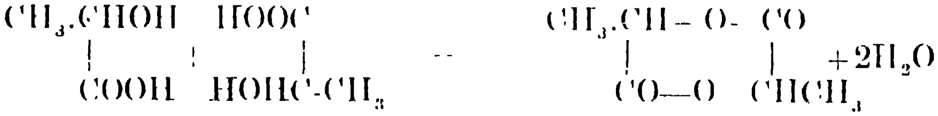
(ii) by hydrolysis of acetaldehyde cyanhydrin (p. 36).

$$CH_3CH(OH)CN + 2H_2O = CH_3CH(OH)COOH + NH_3$$

Properties.—(i) Lactic acid is a colourless viscid liquid with a sour taste (m.p. 18°). It is highly hygroscopic, and is soluble in water, alcohol and ether.

(ii) It cannot be distilled unchanged at ordinary pressure, as it decomposes into CH_3CHO, CO and water; but it distils unchanged at 1 mm. pressure. $CH_3CH(OH)COOH = CH_3CHO + H_2O + CO$

(iii) It forms a *lactide* (a cyclic diester) on heating by elimination of two molecules of water.



(iv) It decomposes into CH_3CHO and HCOOH on heating with dilute H_2SO_4. With conc. H_2SO_4, CO is evolved.

$$CH_3CH(OH)COOH = CH_3CHO + HCOOH$$

(v) It is a monobasic acid and forms salts and esters as usual, e.g., ethyl lactate, $CH_3CH(OH)COOC_2H_5$.

But the acid also contains a secondary alcoholic group –CHOH, and behaves as such. On oxidation with hydrogen peroxide in presence of ferrous sulphate (Fenton's reagent), it gives pyruvic acid, $CH_3.CO.COOH$. $CH_3.CHOH.COOH + O = CH_3.CO.COOH + H_2O$

Lactic acid also gives iodoform reaction.

Uses. Lactic acid and its salts are used in dying, tanning and calico-printing. Ethyl lactate is a solvent for lacquer varnish. Calcium lactate is used medicinally, for calcium deficiency.

Optical isomerism of lactic acid.—Lactic acid exists in three isomeric forms. All the forms have the same structure and chemical composition and hence the same chemical properties, but they differ in physical properties and in their action on plane polarised light. Such compounds are called **optical isomers** or **stereo-isomers,** and the phenomenon is known as **optical isomerism** or **stereo-isomerism.**

The phenomenon was clearly explained by Le Bel and van't Hoff in 1874. In order to explain optical isomerism it was necessary to represent quadrivalent carbon in three dimensions. The optical isomerism was interpreted in terms of the *arrangement in space* of different atoms or groups linked to the carbon atom.

It was assumed that the carbon atom is situated at the centre of an imaginary regular tetrahedron, and that its four valencies are directed in space in straight lines, drawn from the centre of the tetrahedron towards its four corners, as shown by the dotted lines (fig. 5). The angle between each pair of valency bonds is 109·5° and one pair

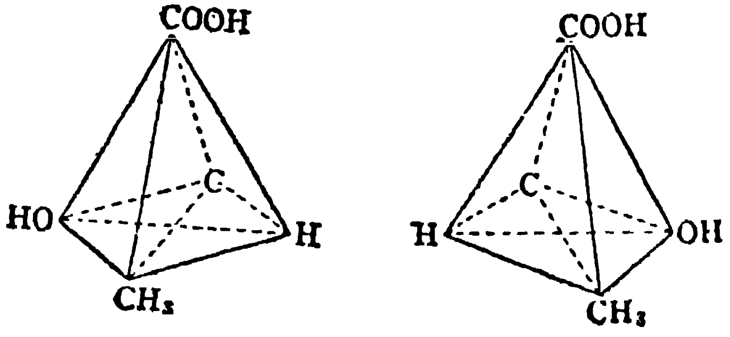
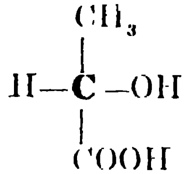


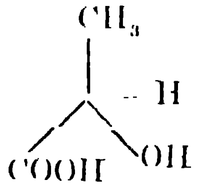
Fig (ii)

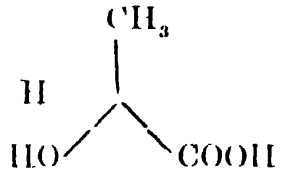
lies in a plane at right angle to the plane of the other pair. Therefore, the valence bonds of a carbon atom are not distributed in one plane. All the four valencies are equally distributed in space.

Now, the space formula of a carbon atom attached to four different atoms or groups, can exist in two, but only two, different forms and they are related as an object to its mirror-image. Both the structures are asymmetric, i.e., they have no plane of symmetry. Lactic acid can exist in two such asymmetric forms, since it contains in its molecule an **asymmetric carbon** atom (shown in heavy type), i.e., *a carbon atom linked to four different atoms or groups*. The two isomeric forms of lactic acid are shown below:



$$\begin{array}{c} CH_3 \\ | \\ H-\mathbf{C}-OH \\ | \\ COOH \end{array}$$





Le Bel and van't Hoff attributed the optical activity of a compound to the presence of asymmetric carbon atoms in the molecule. Lactic acid exhibits optical activity due to the presence of an asymmetric carbon atom in the molecule. The asymmetry in the molecule is accompanied by optical activity.

Both forms of lactic acid (fig. 5) related as an object to its mirror image, are optically active, but their rotations, though equal in magnitude, are opposite in sign. One form turns the plane of polarised light to the right. This is called **dextro** or **d-lactic acid.** The **sarco-lactic acid** which is found in muscles, is d-lactic acid. The other form which turns the plane of polarised light to the left, is called **laevo** or **l-lactic acid.**

Equimolecular mixture of d- and l- lactic acids is optically inactive, since the dextro-rotation of the d-acid is neutralised by the laevo-rotation of the l-acid. **Sour milk lactic acid** is optically inactive. But it can be resolved into optically active d- and l-lactic acids. Of the three isomeric lactic acids, therefore, two are optically active and one inactive.

Tartaric acid, HOOC-CH(OH)-CH(OH)-COOH, is dihydroxy succinic acid, and is found in grapes, tamarind and in other fruits. But the chief source is grape juice. During fermentation of grape juice a brown crust of acid potassium tartrate, $C_4H_5O_6K$, called *argol*, wine less or tartar, is deposited. Tartaric acid was isolated from argol by Scheele in 1769. The recrystallised argol is known as **cream of tartar.**

In order to prepare tartaric the argol is dissolved in boiling water and is nearly neutralised with chalk, when calcium tartrate is precipitated and potassium tartrate remains in solution.

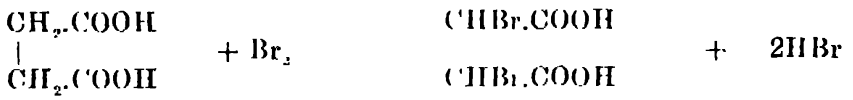
$$\underset{\text{Acid potassium tartrate}}{2C_4H_5O_6K} + CaCO_3 = \underset{\text{Calcium tartrate}}{C_4H_4O_6Ca} + CO_2 + H_2O + \underset{\text{Potassium tartrate}}{C_4H_4O_6K_2}$$

The calcium tratrate is filtered off, and the filtrate is treated with $CaCl_2$ solution, when calcium tartrate is precipitated.

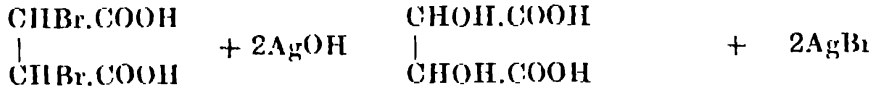
$$C_4H_4O_6K_2 + CaCl_2 = C_4H_4O_6Ca + 2KCl$$

The calcium tartrate is decomposed by dilute H_2SO_4 and the insoluble $CaSO_4$ filtered off—the filtrate on concentration and cooling give crystals of tartaric acid.

Synthesis.—Tartaric acid may be synthesised by the action of moist silver oxide on dibromo-succinic acid. Bromine acts on succinic acid in presence of red P, giving dibromo succinic acid.

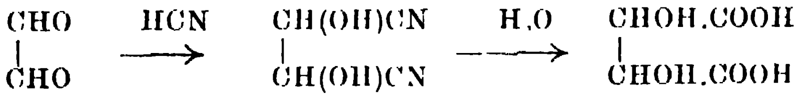


$$\begin{array}{l}CH_2.COOH\\ |\\ CH_2.COOH\end{array} + Br_2 \quad \begin{array}{l}CHBr.COOH\\ \\ CHBr.COOH\end{array} + 2HBr$$



$$\begin{array}{l}CHBr.COOH\\ |\\ CHBr.COOH\end{array} + 2AgOH \quad \begin{array}{l}CHOH.COOH\\ |\\ CHOH.COOH\end{array} + 2AgBr$$

or by the hydrolysis of glyoxal cyanhydrin.

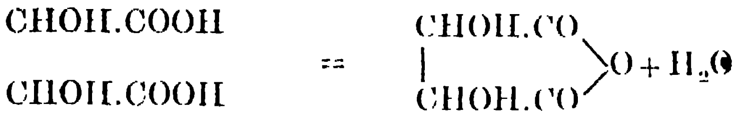


$$\begin{array}{l}CHO\\ |\\ CHO\end{array} \xrightarrow{HCN} \begin{array}{l}CH(OH)CN\\ |\\ CH(OH)CN\end{array} \xrightarrow{H_2O} \begin{array}{l}CHOH.COOH\\ |\\ CHOH.COOH\end{array}$$

Properties.—(i) Tartaric acid is a colourless crystalline solid which is soluble in water and alcohol, but not in ether. The aqueous solution is extremely sour to the taste.

(ii) It is a dibasic acid and hence forms two series of salts and esters. The acid salts e.g., potassium hydrogen tartrata and ammonium hydrogen tartrate, are sparingly soluble in cold water, but the normal salts, such as sodium potassium tartrate (Rochelle salt) is readily soluble in water. *Rochelle salt*, $C_4H_4O_6KNa.4H_2O$, is made by neutralising cream of tartar with sodium carbonate solution and crystallising. *Tartar emetic* (potassium antimonyl tartrate), $C_4H_4O_6K(SbO).H_2O$, a white crystalline solid, moderately soluble in water, is made by boiling aqueous suspension of antimony oxide, Sb_2O_3, with cream of tartar. It is used in medicine as an emetic and as a modrant in cotton dying.

(iii) It forms tartaric anhydride by elimination of a molecule of water, when carefully heated to 150°.



$$\begin{array}{l} \text{CHOH.COOH} \\ \\ \text{CHOH.COOH} \end{array} = \begin{array}{l} \text{CHOH.CO} \\ | \\ \text{CHOH.CO} \end{array}\!\!>\text{O} + H_2O$$

(iv) It reacts with alcohol, giving diethyl tartrate, which with acetyl chloride gives the diacetyl ester.

$$\begin{array}{ll} \text{CHOH.COOC}_2\text{H}_5 & \text{CH(OCOCH}_3\text{).COOC}_2\text{H}_5 \\ \\ \text{CHOH.COOC}_2\text{H}_5 & \text{CH(OCOCH}_3\text{).COOC}_2\text{H}_5 \\ \text{Diethyl tartrate} & \text{Diacetyl diethyl tartrate.} \end{array}$$

(v) HI reduces tartaric acid to succinic acid, but HBr gives dibromo succinic acid.

$$\begin{array}{l} \text{CHOH.COOH} \\ | \\ \text{CHOH.COOH} \end{array} + 4HI = \begin{array}{l} \text{CH}_2\text{COOH} \\ | \\ \text{CH}_2\text{COOH} \end{array} + 2H_2O + 2I_2$$

Tartaric acid is dihydroxy succinic acid.

Tests.—(i) Tartaric acid chars on heating and emits smell of burnt sugar Heating with concentrated sulphuric also chars it, evolving CO, CO_2, etc.

(ii) A neutral solution of a tartrate gives a white precipitate of calcium tartrate on shaking with calcium chloride solution. The precipitate is soluble in acetic acid (cf. calcium oxalate)

(iii) **Silver mirror test.**—An aqueous solution of a tartrate reduces ammoniacal silver nitrate solution on warming, giving a mirror of silver (cf. citrate).

Silver nitrate solution is added to an aqueous solution of Rochelle salt (or any other neutral salt) in a test tube, when a white precipitate of calcium tartrate is formed. The precipitate is just dissolved by adding ammonia soluion drop by drop, and the test tube is then placed in a bath of boling water. A shining mirror of silver is deposited.

Uses.—Tartaric acid is used: (i) as a mordant in dyeing, (ii) in baking powder and in effervescing drinks. Rochelle salt is a constituent of Fehling's solution.

Tartaric acid exists in *four* isomeric forms, all of which have the *same* structure and chemical composition, and hence the same chemical preperties, but they differ in physical properties and in their behaviour towards plane polarised light. The four isomers are.

d-tartaric acid.—The tartaric acid made from argol is d-tartaric acid. It crsytallises in colourless transparent *prisms*, m.p. 170°. It is soluble in water and alcohol, but not in ether. The aqueous solution is *dextro-rotatory*, i.e., turns the plane of palarised light to the right. The ordinary acid is d-tartaric acid.

Racemic acid.—Racemic acid is found as a by-product in the mother liquor from cream of tartar (Latin *racemus*, a bunch of grapes). It forms *rhombic* crystals (m.p. 204°) carrying two molecules of water of crystallisation; d-tartaric acid forms anhydrous prisms, m.p. 170°. Racemic acid is less soluble in water than the d-acid; their salts show similar differences in solubility. It is *optically inactive* but may be resolved into optically active d- and l- tartaric acids. When the d-tartaric acid is heated with water in a sealed tube to 175° or boiled with strong caustic soda soluion, it is converted into racemic acid. The process is called **racemisation.**

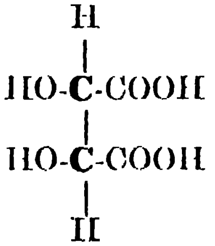
l-tartaric acid resembles d-tartaric acid in all properties except crystalline form and the sign of optical rotation. Its aqueous solution turns the plane of polarised light to the left, and to the same extent as the d-acid, i.e., it is *laevo-rotatory*. A mixture of the d- and l- acids in equal amounts produces no optical rotation and forms racemic acid. The l-tartaric acid is obtained from the racemic acid by resolving into the d- and l- forms.

Meso-tartaric acid is not found in nature but is formed (together with racemic acid) by heating the d-acid with water or aqueous caustic soda in a sealed tube at 165°. Mesotartaric acid (m.p. 140°) crystallises in plates with one molecule of water of crystallisation. It is more soluble than the racemic acid. The calcium meso-tartrate is very much less soluble in water than ordinary calcium tartrate, and is also insoluble in acetic acid. *Meso-tartaric acid is optically inactive.*

Synthetic tartaric acid is optically inactive. It is either a racemic acid or a mixture of racemic and meso-tartaric acids.

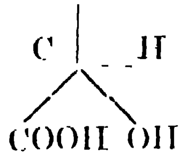
Optical isomerism of tartaric acid.—Tartaric acid exists in four isomeric forms: *two optically active forms*, e.g., d-tartaric acid and l-tartaric acid, and *two optically inactive forms*, e.g. racemic acid and meso-tartaric acid.

An inspection of the structural formula of tartaric acid shows that it contains *two asymmetric carbon atoms* (heavy type), each of which is linked to the *same* set of 4 atoms or groups, namely, H, OH, COOH and CH(OH)COOH. The two asymmetric carbon atoms are exactly identical, and hence their effect on polarised light will be the *same* in magnitude in respect of each carbon atom, and the total optical effect of the molecule is additive.

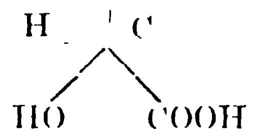


$$\begin{array}{c} H \\ | \\ HO\text{-}\mathbf{C}\text{-}COOH \\ | \\ HO\text{-}\mathbf{C}\text{-}COOH \\ | \\ H \end{array}$$

Let us consider the two asymmetric carbon atoms separately. In the following two arrangements one is the mirror image of the other,

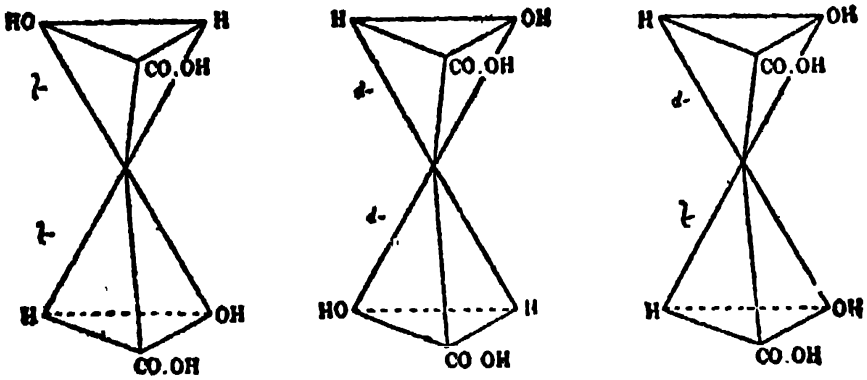


(i)



(ii)

and has, therefore, *equal* but *opposite* effects on plane polarised light.



(i) (ii) (iii)

Fig. 6

Suppose that the arrangement (i) is dextro-rotatory, and therefore, the grouping (ii) is laevo-rotatory. (fig. 6).

(i) When both the asymmetric carbon atoms in a molecule of tartaric acid have detxro rotatory effect, the molecule turns the plane of polarisation to the right, and is known as d-tartaric acid (ii).

(ii) When both the asymmetric carbon atoms in a molecule of tartaric acid have laevo-rotatory effect, the molecule turns the plane of polarisation to the left, and is called the l- tartaric acid (i). The l-acid is a mirror image of the d-acid, and none has a plane of symmetry.

(iii) When one asymmetric carbon atom is dextro-rotatory, and the other laevo-rotatory, the molecule of tartaric acid as a whole has no effect on plane polarised light and is optically inactive. This is meso-tartaric acid. (iii) The dextro-rotatory effect of one carbon atom is just compensated by the laevo-rotatory effect of the other carbon atom. This is *internal compensation.* Meso-tartaric acid cannot be resolved into d- and l-tartaric acids.

(iv) A mixture of *equal* amounts of d- and l-tartaric acids will have no effect on plane polarised light, since the dextro-rotation of the d-acid is just neutralised by the laevo-rotation of the l-acid. The mixture is, therefore, optically inactive. The racemic acid is such a equimolecular mixture of d- and l-tartaric acids, and is also called dl-tartaric acid. It is optically inactive, but can be resolved into optically active d- and l-acids. The racemic acid is therefore, said to be *externally* compensated.

Louis Pasteur, (1850) the famous French scientist, did classical researches on optical isomerism of tartaric acid.

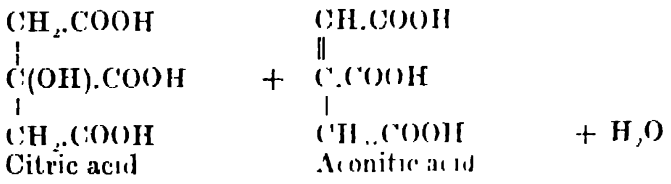
Citric acid, $C_6H_8O_7$, occurs free in citrus fruits (and hence the name) such as lime, lemon, tomato and orange. Scheele isolated the acid from lemon juice in 1784.

Citric acid, is made from lemon juice, which contain 7-8% of the acid, by *boiling* with milk of lime, when calcium citrate is precipitated. The precipitate is separated and decomposed with dilute H_2SO_4. The insoluble $CaSO_4$ is filtered off—the filtrate gives crystals of critic acid on concentration and cooling.

Citric acid is also made by fermentation of a dilute glucose solution at about 40°—the ferment is a fungus which decomposes glucose into citric acid and carbon dioxide. The acid is separated by formation of calcium citrate, as above.

Properties.—(1) Citric acid forms large transparent crystals, $C_6H_8O_7.H_2O$. The crystals melt at 100°, but the anhydrous acid at 153°. It is soluble in water and alcohol, but not in ether.

(ii) When heated to 175°, it loses a molecule of water, formic aconitic acid.



$$\begin{array}{l} CH_2.COOH \\ \vert \\ C(OH).COOH \\ \vert \\ CH_2.COOH \\ \text{Citric acid} \end{array} \quad + \quad \begin{array}{l} CH.COOH \\ \Vert \\ C.COOH \\ \vert \\ CH_2.COOH \\ \text{Aconitic acid} \end{array} \quad + H_2O$$

Citric acid is a monohydroxy-tricarboxylic acid

(iii) It is optically inactive, as it contains no asymmetric carbon atom in the molecule.

(iv) It does not reduce ammonical silver nitrate on warming, but slight reduction takes place on boiling (*cf.* tartrates).

(v) A neutral solution of a citrate gives a white precipitate of calcium citrate on *boiling* with $CaCl_2$ solution. (*cf.* tartrates). Calcium citrate is soluble in cold but insoluble in boiling water.

Uses.—Citric acid is used in making lemonades and as a mordant in dyeing. Ferric-ammonium citrate is used in medicine.

XIV

CARBOHYDRATES

The Carbohydrates.—Sugar, starch and cellulose which are the important products of plant life, are the common examples of a class of substances, known as *carbohydrates*. The name carbohydrate originated from the fact that compounds belonging to this class, contain carbon, hydrogen and oxygen only, the hydrogen and oxygen being in the ratio of 2:1 (as in water), and their formula may be writen as $C_x (H_2O)_y$, i.e., hydrate of carbon, e.g., glucose $C_6(H_2O)_6$ or $C_6H_{12}O_6$; cane sugar $C_{12}(H_2O)_{11}$ or $C_{12}H_{22}O_{11}$. But the term is misleading as carbohydrates do not behave as hydrates. Also, carbohydrates are known which do not contain carbon and hydrogen in the ratio of 2:1, e.g., rhamnose, $C_6H_{12}O_5$.

The carbohydrates fall into two main groups: the sweet and crystalline sugars, e.g., glucose and cane sugar, and the tasteless and amorphous *starch* (as rice, wheat, barley, potato, etc.) and *cellulose* (as cotton, grass, straw, wood, bamboo, jute, etc.).

The carbohydrates are classified, by reference to their behaviour towards hydrolysis, into:

(i) **Monosaccharides** which do not undergo hydrolysis with dilute acids, e.g., glucose, $C_6H_{12}O_6$, and fructose, $C_6H_{12}O_6$.

(ii) **Disaccharides,** $C_{12}H_{22}O_{11}$, which give two molecules of monosaccharides on hydrolysis, e.g., can sugar and lactose.

$C_{12}H_{22}O_{11}$ (cane sugar) + H_2O = $C_6H_{12}O_6$ (glucose) + $C_6H_{12}O_5$ (fructose).

(iii) **Polysaccharides,** $(C_6H_{10}O_5)_n$, which on hydrolysis give monosachharide, *e.g.*, starch, cellulose, gum, pectin, and dextrin, etc.

The **tri-** and **tetra-saccharides,** on hydrolysis, give 3 and 4 monosaccharides-respectively.

The monosaccharides are either polyhydroxy aldehydes or polyhydroxy ketones, and are known as *aldose* and *ketose* respectively. Glucose, $C_6H_{12}O_6$, is *aldo-hexose*, and *fructose*, $C_6H_{12}O_6$, is *keto-hexose*. The ending *-ose* generally refers to carbohydrates.

Carbohydrates are mainly derived from the vegetable kingdom. The carbohydrates are of great importance in our daily life. The starchy food we take, the cotton fabrics we wear, or the paper we write on, are all carbohydrates. Cotton is almost pure cellulose. Paper is made from bamboo and grass which are mainly cellulose. The carbohydrate, chiefly starch, is one of main types of foodstuffs which are *fats*, *proteins* and *carbohydrates*. Alcohol is made from carbohydrates. Artificial silk and celluloid are produced from modified cellulose.

Glucose, $C_6H_{12}O_6$, occurs in grapes—ripe grapes may contain as high as 20-30 per cent of it. But it also occurs in most ripe fruits, in the nectar of flowers, and in honey, usually associated with fructose and cane sugar. It is called **grape sugar** from its presence in grapes, *dextrose* from its dextro-rotation, and *glucose* from its sweet taste (Greek *glucus*, sweet).

Glucose occurs in traces, about 0·1 per cent, in our blood and urine. But in the case of diabetic patients who cannot decompose starch beyond glucose stage due to defects in digestive system, the urine may sometimes contain 8-10% glucose.

In the laboratory glucose can be readily prepared from cane sugar. The can sugar is dissolved in 90 per cent alcohol and the solution warmed with strong hydrochloric acid, when the cane sugar is converted into glucose and fructose. Fructose, being more soluble in alcohol, remains in solution, while glucose separates as anhydrous crystals. $C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6$ (glucose) $+ C_6H_{12}O_6$ (fructose).

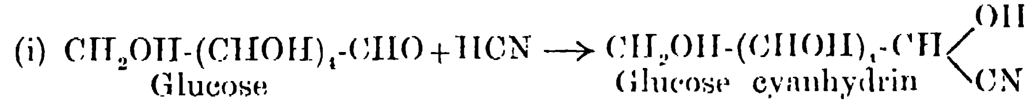
Glucose is made *commercially* from starch (which is built up of a large number of glucose molecules). Starch is hydrolysed into glucose by heating with dilue H_2SO_4 under pressure.

$$(C_6H_{10}O_5)_n\text{(starch)} + nH_2O = nC_6H_{12}O_6.$$

The liquid is neutralised with chalk and the insoluble $CaSO_4$ filtered off—the aqueous solution of glucose is then decolorised by filtration through a bed of animal charcoal, and then concentrated to a thick syrup in a vacuum pan.

Properties. —(i) Glucose is a colourless crystalline solid with a sweet taste, though not as sweet as cane sugar. It is readily soluble in water, but only sparingly soluble in alcohol. It crystallises from aqueous solution with one molecule of water, the crystals melt at 86° ; the anhydrous crystals melt at 146°. Glucose is dextro-rotatory in aqueous solution. It is fermnted by yeast to alcohol and CO_2.

(ii) Glucose contains 5 alcoholic OH groups and one aldehyde group, -CHO, in its molecule. Glucose is *aldohexose*. It gives many reactions of aldehydes. Thus it forms cynhydrin with HCN, oxime with hydroxylamine, NH_2OH, and phenylhydrazone with phenyl hydrazine, $C_6H_5NH.NH_2$. The reactions are :



$$\text{(i)}\ \underset{\text{Glucose}}{CH_2OH\text{-}(CHOH)_4\text{-}CHO} + HCN \longrightarrow \underset{\text{Glucose cyanhydrin}}{CH_2OH\text{-}(CHOH)_4\text{-}CH}\begin{smallmatrix} OH \\ CN \end{smallmatrix}$$

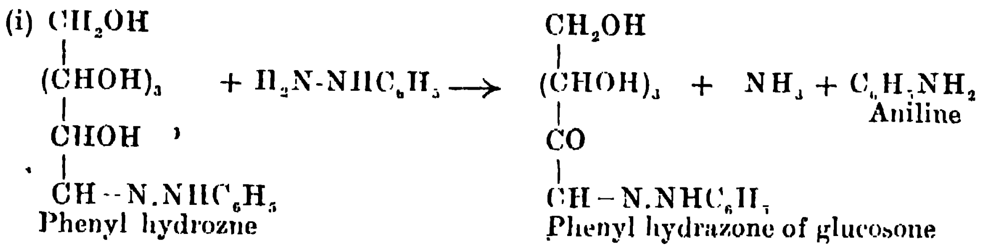
$$\text{(ii)}\ CH_2OH\text{-}(CHOH)_4\text{-}CHO + H_2NOH \longrightarrow \underset{\text{Glucose oxime}}{CH_2OH\text{-}(CHOH)_4\text{-}CH = NOH} + H_2O$$

$$\text{(iii)}\ CH_2OH\text{-}(CHOH)_4\text{-}CHO + H_2N\text{-}NHC_6H_5 \longrightarrow \underset{\text{Glucose phenyl hydrazone}}{CH_2OH\text{-}(CHOH)_4\text{-}CH = N\text{-}NHC_6H_5} + H_2O$$

But the phenyl hydrazone by further action of phenyl-hydrazine forms a yellow crystalline solid with a definite melting point, known as *glucosazone*.

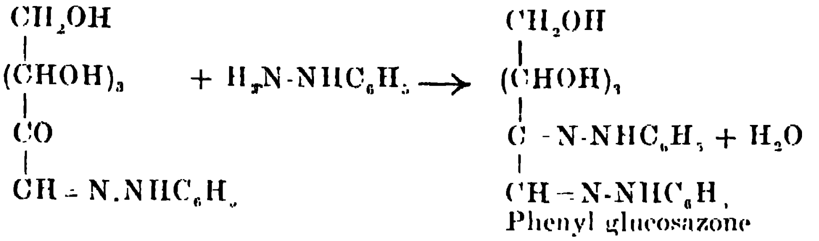
The phenyl hydrazone is oxidised by a second molecule of phenyl hydrazine, giving a ketone which is phenyl hydrazone of glucosone ; the ketone reacts with a third molecule of phenyl hydrazine, forming glucosazone :

(i)



$$\begin{array}{l} CH_2OH \\ | \\ (CHOH)_3 \\ | \\ CHOH \\ | \\ CH{-}N.NHC_6H_5 \\ \text{Phenyl hydrozne} \end{array} + H_2N\text{-}NHC_6H_5 \longrightarrow \begin{array}{l} CH_2OH \\ | \\ (CHOH)_3 \\ | \\ CO \\ | \\ CH{-}N.NHC_6H_5 \\ \text{Phenyl hydrazone of glucosone} \end{array} + NH_3 + \underset{\text{Aniline}}{C_6H_5NH_2}$$

(ii)

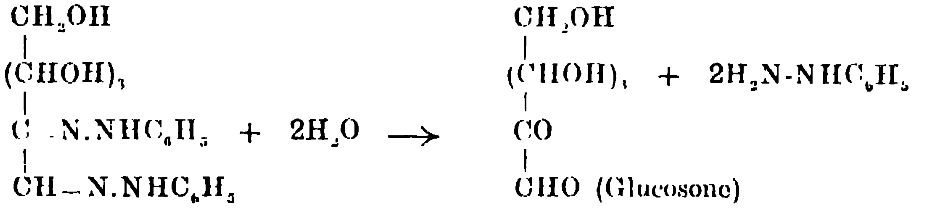


$$\begin{array}{l} CH_2OH \\ | \\ (CHOH)_3 \\ | \\ CO \\ | \\ CH{=}N.NHC_6H_5 \end{array} + H_2N\text{-}NHC_6H_5 \longrightarrow \begin{array}{l} CH_2OH \\ | \\ (CHOH)_3 \\ | \\ C{=}N\text{-}NHC_6H_5 \\ | \\ CH{=}N\text{-}NHC_6H_5 \\ \text{Phenyl glucosazone} \end{array} + H_2O$$

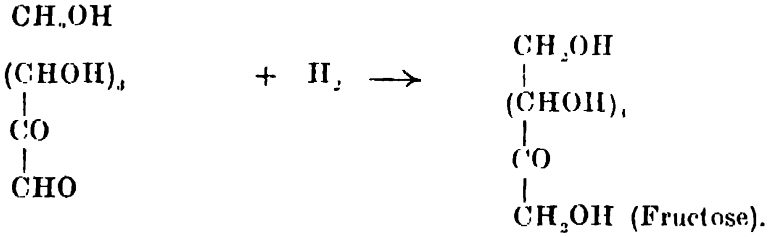
The osazone is used in *detecting* and *identifying glucose*.

Formation of osazone —A solution of phenyl hydrazine acetate (prepared by mixing 1 gm. of phenyl hydrazine with 1 gm. of glacial acetic acid, and then diluting to 10 c.c.) is added to 5 c.c. of glucose solution (containing about 0·5 gm. glucose). The mixture is heated in a test tube in a bath of boiling water. In 10-15 minutes yellow crystals of osazone separate. The crystals are filtered, washed with water and recrystallised from alcohol. The osazone melts at 204·5°, and looks like crystalline tufts under the microscope.

Conversion of glucose into fructose.—On hydrolysis with hydrochloric acid phenyl glucosazone gives glucosone. The glucosone on reduction with zinc dust and acetic acid yields fructose :



$$\begin{array}{l} CH_2OH \\ | \\ (CHOH)_3 \\ | \\ C{=}N.NHC_6H_5 \\ | \\ CH{-}N.NHC_6H_5 \end{array} + 2H_2O \longrightarrow \begin{array}{l} CH_2OH \\ | \\ (CHOH)_3 \\ | \\ CO \\ | \\ CHO\ \text{(Glucosone)} \end{array} + 2H_2N\text{-}NHC_6H_5$$



$$\begin{array}{l} CH_2OH \\ | \\ (CHOH)_3 \\ | \\ CO \\ | \\ CHO \end{array} + H_2 \longrightarrow \begin{array}{l} CH_2OH \\ | \\ (CHOH)_3 \\ | \\ CO \\ | \\ CH_2OH\ \text{(Fructose).} \end{array}$$

(iii) Like aldehydes, glucose reduces ammoniacal silver nitrate and Fehling's solution (p. 38).

(a) A mirror of silver deposits on adding a solution of glucose to ammoniacal silver nitrate solution in a test tube and then heating the test tube in boiling water:

$$CH_2OH\text{-}(CHOH)_4\text{-}CHO + Ag_2O \longrightarrow \underset{\text{Gluconic acid}}{CH_2OH\text{-}(CHOH)_4\text{-}COOH} + Ag$$

(b) A red precipitate of cuprous oxide is formed on boiling a solution of glucose with Fehling's solution. The reaction is used in the *estimation* of sugar, and also for *detecting* reducing sugar in the urine of diabetic patients.

$$CH_2OH\text{-}(CHOH)_4\text{-}CHO + 2CuO \longrightarrow CH_2OH\text{-}(CHOH)_4\text{-}COOH + Cu_2O$$

(iv) On mild oxidation with bromine water glucose gives gluconic acid, $C_6H_{12}O_7$—the aldehyde group -CHO, in glucose, being oxidised to -COOH group. Gluconic acid on further oxidation gives saccharic acid. Strong nitric acid, however, oxidises glucose to oxalic acid.

$$\text{(i)}\ CH_2OH\text{-}(CHOH)_4\text{-}CHO + Br_2 + H_2O \longrightarrow \underset{\text{Gluconic acid}}{CH_2OH\text{-}(CHOH)_4\text{-}COOH} + 2HBr$$

$$CH_2OH\text{-}(CHOH)_4\text{-}COOH + O_2 \longrightarrow \underset{\text{Saccharic acid}}{HOOC\ (CHOH)_4\text{-}COOH} + H_2O$$

$$\text{(ii)}\ CH_2OH\text{-}(CHOH)_4\text{-}CHO + 9\ O \longrightarrow 3\ \underset{\text{Oxalic acid}}{HOOC\text{-}COOH} + 3H_2O$$

(v) Glucose forms a penta-acetyl derivative, $C_6H_7O(OCOCH_3)_5$, by reaction with acetic anhydride, and hence it contains 5 OH groups:

$$\underset{\text{Glucose}}{CH_2OH-(CHOH)_4-CHO} + CH_4COCl \longrightarrow \underset{\text{Penta acetyl glucose}}{CH_2(OCOCH_3)\ (CHOCOCH_3)_4\text{-}CHO} + 5HCl$$

Glucose is, therefore, penta-hydroxy aldehyde, $C_5H_6(OH)_5.CHO$.

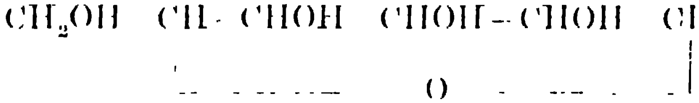
(vi) Glucose is reduced by sodium-amalgum to an alcohol *sorbitol*, the CHO group being reduced to the CH_2OH group:

$$\underset{\text{Glucose}}{CH_2OH-(CHOH)_4\ CHO} + 2H \longrightarrow \underset{\text{Sorbitol}}{CH_2OH\text{-}\ (CHOH)_4\text{-}\ CH_2OH}$$

The sorbitol on reduction with HI gives *normal* secondary hexyl iodide, $CH_3\text{-}CHI\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$, which is a derivative of normal hexane, $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$. Therefore, glucose is a straight chain compound and may be written as:

$$CH_2OH-CHOH-CHOH\ CHOH-CHOH--CHO$$

But the open chain formula of glucose cannot strictly explain its behaviour. It has been established that glucose exists in a cyclic form and that it contains an oxide ring in its structure:



$$CH_2OH\ \ \underbrace{CH\text{-}\ CHOH\ \ CHOH-CHOH\ \ CHOH}_{O}$$

(vii) On heating alone or with strong H_2SO_4, glucose chars into a black mass.

Molisch's test.—Two to three drops of an alcoholic solution of α-naphthol is added to glucose solution and then conc. H_2SO_4 is carefully poured down the side of the test tube—a blue or violet colour develops. The reaction is given by all soluble carbohydrates.

Uses.—Glucose is used as a sweetening agent in confectionary, and in preserved fruits and jams. It is used in silvering mirrors, and as an invalid food. Patients are given glucose injection to increase the blood sugar content Calcium gluconate removes calcium deficiency Glucose is fermented to wind and beer.

Fructose, $C_6H_{12}O_6$.—Mixed with glucose, it occurs in many fruits (and therefore, also called **fruit sugar**) and in honey. It is also called laevulose, on account of its laevo-rotation in solution.

Preparation.—Fructose may be made from cane sugar by hydrolysis by heating with dilute sulphuric acid. Cane sugar is converted into glucose and fructose. The acid is precipitated as $BaSO_4$ by adding barium carbonate and filtered off. The filtrate is concentrated and heated with milk of lime, when calcium fructosate, $C_6H_{12}O_6.CaO$, being sparingly soluble, separates—calcium glucosate is soluble in water. This is suspended in water and decomposed by CO_2, and filtered from calcium carbonate:

$$C_6H_{12}O_6.CaO + CO_2 = C_6H_{12}O_6 + CaCO_3$$

The filtrate on concentration deposits crystals of fructose.

Commercially, fructose is made from *inulin*, (a polysaccharide made of fructose only) found in dahlia tubers and Jerusalem artichoke. Inulin on hydrolysis with dilute sulphuric acid gives fructose. The acid is removed by precipitation with $BaCO_3$, and the filtrate is evaporated under reduced pressure to a thick syrup, which solidifies on adding a crystal of fructose.

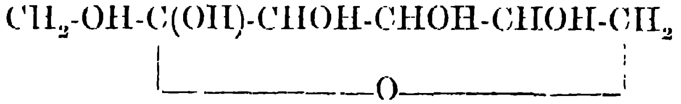
Properties. —Fructose crystallises from alcohol in rhombic prisms, m.p. 95°. It is more soluble in water and alcohol than glucose, and tastes sweeter than glucose. Like glucose, it is fermentable by yeast to alcohol and CO_2.

Fructose contains a ketonic group, $>C=O$, and is therefore, a *ketohexose*. In most of its reactions it resembles glucose. It reacts with HCN, NH_2OH and $C_6H_5NHNH_2$ in the same way as glucose. With phenylhydrazine it gives the *same* osazone as glucose.

Although it is not an aldehyde but a ketone, yet it reduces ammoniacal silver nitrate and Fehling's solution, like glucose. The presence of easily oxidisable $-COCH_2OH$ group in fructose accounts for its reducing property. Fructose, being laevo-rotatory, differs from glucose in its action on polarised light. It forms a penta acetyl derivative like glucose, and hence contains five OH groups. Therefore its structure may be written as $C_5H_7(OH)_5(>CO)$. Like glucose, fructose contains a chain of six carbon atoms, and its formula may be written as:

$$CH_2OH-CHOH-CHOH-CHOH-CO-CH_2OH$$

But it has been shown that fructose exists in a cyclic form and contains an oxide-ring structure:



$$\underbrace{CH_2\text{-}OH\text{-}C(OH)\text{-}CHOH\text{-}CHOH\text{-}CHOH\text{-}CH_2}_{O}$$

• Fructose can be assimilated by diabetic patients, whereas glucose passes out unchanged with urine. They are, therefore, given fructose in place of glucose or cane sugar.

Cane sugar, sucrose, $C_{12}H_{22}O_{11}$, occurs in large quantities in ripe sugar cane (15-18 per cent) and in beet root (15-25 per cent), and also in small quantities in some fruits such as pineapples, strawberries and ripe banana. Sugar is obtained commercially from either *sugar cane* or *sugar beet*.

Extraction from sugar cane. —The sugar canes are cut into short length, and pressed between hot rollers, whereby the juice is expressed. The juice contains about 10-20 per cent cane sugar and a reducing sugars (glucose, etc.). It is heated at about 90° with excess of milk of lime in order to precipitate as insoluble calcium salts the phosphoric, oxalic and citric acids, and to coagulate the albumin, which are contained in the juice. Carbon dioxide is then passed through the liquid to precipitate the excess of lime, and also to decompose the *saccharate of lime*, $C_{12}H_{22}O_{11}.3CaO$, which is formed

$$C_{12}H_{22}O_{11}.3CaO+3CO_2 = C_{12}H_{22}O_{11}+3CaCO_3.$$

The precipitate is removed by filtration. The filtered juice is decolorised by passing in *sulphur dioxide*. The clear juice is then concentrated under reduced pressure in vacuum evaporators, until the syrupy liquid deposits large crystals on being cooled. It is then run out and cooled, when sugar crystallises out. The crystals are separated from the yellow (or brown) syrupy *mother liquor* (called molasses) by a centrifuge.

(ii) **Extraction from sugar beet.**—The discovery of sucrose in beet root was by the German chemist Marggraf in 1747. The sugar content originally was about 7 per cent only, but it has been raised as high as 25 per cent by careful breeding, but the average is 16 per cent. The roots are washed to remove any adhering earth, and cut into thin slices, and then macerated with hot water. The aqueous extract of sugar is then treated in the same way as sugar cane juice.

Molasses is used in making alcohol (p. 27), and also as a cattle food and a fertiliser. *Begasse* (the extracted canes) is used as a fuel and in making the building board 'celotex'.

Sugar refining.—The raw cane sugar has a brown or yellow colour. It is refined by dissolving in water and then filtering the solution through beds of animal charcoal. The decolorised solution is then evaporated under reduced pressure and crystallised.

The name cane sugar and beet sugar merely refers to the source of the sugar. Chemically they are identical, and refer to a single chemical substance sucrose. Cane sugar is the commercial name for sucrose.

Properties.—Sugar crystallises from aqueous solution in monoclinic prisms. *Surgar candy* is large sugar crystals deposited on threads suspended in the solution.

Sugar is readily soluble in water but is almost insoluble in alcohol. It melts at 160° and on cooling sets to a pale yellow glassy mass, known as *barley sugar*. But at about 200° it is converted into a brown mass, known as *caramel*, which is much used in confectionary, and for tinting spirits, soups and vinegar, etc. A very pure form of charcoal, known as *sugar charcoal*, is prepared by dry distillation of sugar.

Sucrose is optically active and is dextro-rotatory. The concentration of sucrose in a solution can be measured by determining its rotation in a polarimeter. Sucrose is readily hydrolysed by warming with dilute mineral acids, e.g., dilute H_2SO_4, into glucose and fructose.

$$C_{12}H_{22}O_{11}+H_2O = C_6H_{12}O_6+C_6H_{12}O_6$$

The mixture is known as **invert sugar,** and the process **inversion of sucrose.** Of the two sugars formed, glucose is dextro-rotatory and fructose laevo-rotatory but the rotation of fructose is greater than that of glucose, and therefore, the invert sugar is laevo-rotatory. But since cane sugar is dextro-rotatory, this process of hydrolysis is called *inversion* due to change of sign in the rotation. The invert sugar is sweeter than cane sugar and is used in confectionary, and also as a food for the infants and the invalid.

Concentrated sulphuric acid gradually decomposes and chars sugar—the charred mass froths up. Concentrated nitric acid converts it into oxalic acid. Sucrose is not directly fermentable by yeast. Before alcoholic fermentation, it undergoes inversion by the enzyme *invertase*, also present in yeast.

Sucrose does not show reactions of an aldehyde or a ketone. It is not a reducing sugar. It does *not* reduce Fehling's solution, but does so after boiling with dilute sulphuric acid for a few minutes, when inversion into glucose and fructose takes place. By this reaction sucrose can be *detected* and *distinguished* from the reducing sugars, e.g., glucose and fructose, which *directly reduce* Fehling's solution.

Test.—A solution of cane sugar is inverted by boiling with dilute sulphuric acid, and then made alkaline with caustic soda solution, and boiled with Fehling's solution. A red precipitate of cuprous oxide is formed and detects cane sugar.

Cane sugar is an important article of food.

Polysaccharides.—Starch and cellulose are complex carbohydrates built up from a large number of glucose (monosaccharide) molecules with elimination of water. They are called polysaccharides and give glucose on acid hydrolysis. Their molecular complexity is not definitely known, and hence their formula is given as $(C_6H_{10}O_5)_n$. In contrast to simple sugars, they are tasteless amorphous substances which are insoluble in water.

Starch, amylum, $(C_6H_{10}O_5)_n$, occurs in various parts of plants particularly in seeds, roots, and tubers (where it forms the food reserve for growing plants). All kinds of grain such as rice (75%), maize (65-70%) and tubers such as potato (20%), tapioca, and arrowroot, contain starch, and are its chief sources. The extraction of starch is a mechanical process. The starch-bearing material is finely crushed (so as to break the cell-walls and release the starch) and mixed with water, and then passed through seives which allows the starch granules to pass through but not the coarse particles of cell tissue. The starch granules are allowed to settle and then separated by centrifuging and dried.

Sago starch is made from the pith of sago palm.

Properties. Starch is insoluble in water, but when heated with water, the starch granules swell and burst, giving an opaque solution, which sets to a stiff paste, known as *starch paste*, on cooling. Starch paste is used in stiffening linen, in sizing paper and as adhesives.

A solution of starch is best made by rubbing starch into a paste with cold water, and then pouring the paste into boiling water.

A solution of starch gives a deep blue colour with iodine solution. The colour disappears on heating and reappears on cooling. This is a *delicate test* for starch as also for iodine. When heated with dilute mineral acids, starch is converted into a gummy mass, called *dextrin*, by partial hydrolysis, but prolonged action of the acid gives *maltose*, $C_{12}H_{22}O_{11}$, and finally glucose, by complete hydrolysis:

$$\text{Starch} \longrightarrow \text{dextrin} \longrightarrow \text{maltose} \longrightarrow \text{glucose.}$$

Diastase (p. 27) also converts starch into maltose, so also *saliva* and *pancreatic juice* (which contains *ptyalin* resembling diastase). *Takadiastase* converts starch into glucose, and is given to patients for digestion of starchy food. *Dextrin* is prepared by heating starch to about 200°, and is used as adhesive under the name *British gum*. Starch is an important food stuff. It is used in making glucose, alcohol and adhesives, and in stiffening linen and sizing paper, and for laundry purposes.

Cellulose, $(C_6H_{10}O_5)_n$, like starch, is widely distributed throughout the vegetable world and is the most abundant of all organic compounds. It is the chief component of the cell-wall of plants, and forms the frame work of all the vegetable tissues. Cotton, linen and filter paper are nearly pure cellulose. Cellulose is usually found as fibres which are suitable for spinning and paper-making. Wood, jute, hemp, flax, and straw, etc., contain cellulose which is associated with lignin, gum and resin, etc.

Cellulose is insoluble in water and is fairly resistant to the action of alkalis and chlorine, and also dilute acids. Its inertness towards common reagents accounts for its use as a filter paper. Caustic soda and chlorine are often used in getting cellulose freed from the impurities like lignin, etc. In making **paper,** for example, from wood, bamboo, grass, etc., the raw material is boiled with caustic soda solution to dissolve out the lignin, etc., and then bleached with sodium hypochlorite. The bleached cellulose is then pressed into paper sheets with the addition of *sizing* material (alum, rosin, china clay, etc) which makes the paper impervious to ink.

Fuming hydrochloric acid or boiling dilute H_2SO_4 converts cellulose into glucose only. The reaction shows that cellulose is made up of glucose units only. Wood may be similarly converted into glucose. When cellulose, e.g., unsized paper (filter paper), is dipped into 80 per cent sulphuric acid, it becomes tough and translucent. When washed with water, then ammonia, and finally dried, it becomes smooth and impervious and is known as *parchment paper*.

When cotton fibres are treated under tension with 20 per cent caustic soda solution, they become glossy and develop a silky lustre. The process is known as **mercerisation** after John Mercer who discovered the process in 1884.

When heated with a mixture of HNO_3 and H_2SO_4, cellulose gives a series of cellulose nitrates commonly called **nitrocellulose.** Highly nitrated cellulose, e.g., **gun cotton,** is used in making explosives. Gun cotton is insoluble in a mixture of alcohol and ether, but is soluble in acetone forming a jelly. The acetone solution is mixed with nitroglycerine and vaseline to prepare **cordite** (*smokeless powder* for the military). **Blasting gelatine** is a mixture of gun cotton and nitroglycerine. Less highly nitrated cellulose is known as **pyroxylin** and is soluble in a mixture of alcohol and ether. The solution is known as **collodion,** and is used in making artificial silk, and in medicine and photography. Pyroxylin is mixed with camphor and alcohol and converted into **celluloid** by heat and pressure. Celluloid is tough and transparent, and is readily moulded when hot, and is used for making combs, knife handles, imitation ivory and tortoise shells, etc. It is highly inflammable.

Cellulose dissolves in a solution of copper hydroxide in ammonia. The solution is used in making artificial silk.

Cotton and wood cellulose are largely used for making **artificial silk** or **rayon.** *Rayon* is chiefly made by the *viscose process*. In this method the cellulose (wood pulp) is treated with strong caustic soda solution, and then carbon disulphide when a viscous mass, called *viscose* (cellulose xanthate) results. The viscose is dissolved in dilute aquous caustic soda, and the resulting solution is forced through sets of fine jets into a bath of dilute sulphuric acid, when cellulose regenerates, forming fine threads. The yarn is then bleached and dried.

Celluloso acetate is also used in making rayon, known as **celanese.** Cellulose acetate rayon is superior to viscose rayon in its resistance to moisture. Rayon is celluloso fibre, but wool and silk are protein fibres and therefore, emit a smell of burnt hair on ignition, as they contain sulphur.

Cellophane paper is made from viscose solution in the same way as viscose rayon. It is used as wrapping paper.

Nylon is a synthetic fibre but it is not a cellulose derivative.

XV

AROMATIC COMPOUNDS

Benzene and its Homologues

Aromatic hydrocarbons.—A small group of plant products such as gum benzoin, tolu balsam, oil of bitter almonds and oil of winter-green, etc., was originally classified as *aromatic* because of the fragrant smell or *aroma* they all possess in common.

The aromatic compounds contain a higher percentage of carbon than the corresponding aliphatic hydrocarbons and burn with a smoky flame. Thus, benzene, C_6H_6, the simplest aromatic hydrocarbon, contains 93·6 per cent, whereas hexane, C_6H_{14}, contains 83·7 per cent carbon.

Experiment.—Burn some benzene and hexane in two porcelain basins and observe the much larger deposit of soot in the benzene flame.

Most of the simple aromatic compounds contain at least *six* carbon atoms. The more complex aromatic compounds may be converted by the action of appropriate reagents into the simplest aromatic hydrocarbon benzene, C_6H_6 or its derivatives. But any attempt to convert an aromatic compound into compounds with fewer carbon atoms than six (as in benzene) disrupts the entire molecule. Benzene is, therefore, regarded as the parent substance of all aromatic compounds Compounds derived from or closely related to benzene are now called aromatic to distinguish them from aliphatic compounds. They are cyclic or ring compounds *containing at least one benzene ring.*

Coal tar.—Coal tar is the principal source of benzene and many other aromatic compounds such as toluene, xylene, naphthalene and carbolic acid, etc. Synthetic organic dyestuffs are aromatic compounds. The discovery of the first synthetic coal tar colour *mauve* by W. H. Perkin in 1856 gave a stimulus to the study of coal tar products which largely helped the development of aromatic chemistry.

The dry distillation of coal at high temperature (1000°-1400°) yields coal tar (about 5 per cent of coal), ammoniacal liquour (8 per cent), coal gas (70 per cent) and coke (17 per cent).

Coal tar is a thick, black oily liquid (sp. gr. 1·1-1·2) with unpleasant smell. Water is removed from the tar by slow heating and the tar is then distilled in iron retorts—the distillate is collected in a number of fractions in separate receivers according to specific gravity or temperature at which the fraction is collected. The fractions are :

Temperature range	Number of fractions	Sp. gr.	Yield by volume
Upto 170°	Light oil or crude naphtha	0·970	2-8 per cent.
170° to 230°	Middle oil or carbolic oil	1·005	8-10 ,, ,,
230° to 270°	Heavy oil or creosote oil	1·033	8-10 ,, ,,
270° to 360°	Green oil or anthracene oil	1·088	16-20 ,, ,,
—	Pitch (left in still)	—	55-60 ,, ,,

These fractions are then worked up and separated into their constituents. The major constituents of different fractions are :

Light oil	Middle oil	Heavy oil	Green oil
Benzene, C_6H_6 Toluene, $C_6H_5.CH_3$ Xylene, $C_6H_4.(CH_3)_2$	Phenol, C_6H_5OH Naphthalene, $C_{10}H_8$	Cresols, $C_6H_4(CH_3)OH$	Anthracene, $C_{14}H_{10}$ Phenanthrene, $C_{14}H_{10}$

The creosote oil is not separated into its constituents and is used as such for preserving timber. The pitch finds uses in roofing and road-making. Naphthalene, a white crystalline solid, m.p. 79°, is used in making dyestuffs (alizarin) and solvents (tetralin and decalin). It acts as a vermin-killer and as a mild antiseptic, and is commonly sold as balls for use as a protection against moths. Anthracene, a colourless solid with a bluish fluorescence, m.p. 216°, is used in making dyes. The coal tar hydrocarbons are the starting point for the synthesis of many dyes, drugs, photographic developers, explosives, flavours and perfumes.

100 parts of tar yield the following approximate quantities of products: benzene 1·6, toluene 0·25, xylene 0·03, phenol 2, naphthalene 4, creosote oil 24, anthracene 02 and pitch 55 parts.

Isolation of benzene.—The crude light oil is re-distilled and the distillate below 70° is rejected. The rest of the distillate is washed successively with strong sulphuric acid, water, caustic soda and water. The sulphuric acid removes the basic impurities, e.g., aniline and pyridine, and also some thiophene; caustic soda removes carbolic acid. The washed light oil is then distilled using a fractionating column; the distillate is collected in three fractions—namely, from 80-100°, 110-140° and 140-170° respectively. The first and second fractions are commercially known as *'90 per cent benzol'* and *'50 per cent benzol'* respectively—the term refers to the proportion of distillate which 100 c.c. of the commercial product yields on distillation below 100°. The 'fifty per cent benzol' contains about 46 beneenze, together with some toluene and xylene. The third fraction is called **solvent naphtha** or **benzine** (consists mainly of xylene, etc.) and is used as a solvent for rubber, paints and resins, etc. The '90 per cent benzol' (which contains 70 per cent benzene, 24 per cent toluene and a little xylene) yields commercial benzene, toluene and xylene on careful fractionation. For further purification, the commercial benzene is cooled in freezing mixture, when pure benzene crystallises out. *Even then, it contains trace of thiophene,* C_4H_4S.

The presence of thiophene in coal-tar benzene may be shown by shaking a little of the benzene with a drop of concentrated sulphuric acid and a crystal of isatin, when a deep blue colour of *indophenin* is produced. No such colour is given by benzene made from benzoic acid.

Thiopene may be removed from coal-tar by agitation with small amounts of cold concentrated sulphuric acid.

Benzene, toluene and xylene are commercially known as benzol, toluol, and xylol respectively.

Benzene, C_6H_6, is the simplest of the aromatic compounds. It was discovered by Faraday in 1825 in the illuminating gas made from whale oil. It was isolated from coal tar by Hofmann in 1845.

Bertholet first synthesised it in 1870 by passing acetylene through a red-hot tube.

$$3C_2H_2 = C_6H_6$$

Commercial benzene is obtained from the light oil fraction of coal tar.

It can be made in the laboratory by distilling benzoic acid or its salt (sodium or calcium benzoate) with soda lime (*cf.* preparation of methane, p. 333).

Experiment.—Mix sodium benzoate with twice its weight of sodalime, and distil the mixture from a retort attached to a condenser and receiver. Wash the oily distillate (smelling strongly of benzene) with water in a tap-funnel, dry with anhydrous calcium chloride and re-distil.

$$C_6H_5COONa \text{ (sodium benzoate)} + NaOH = C_6H_6 + Na_2CO_3.$$

Benzene is also obtained by distilling phenol with zinc dust:

$$C_6H_5OH + Zn = C_6H_6 + ZnO.$$

Properties of benzene.—Benzene is a colourless liquid (b.p. 80·4° and m.p. 5·1°) with a peculiar but not unpleasant smell. It is very inflammable and burns with a smoky flame. It is lighter than water (sp. gr. 0·874 at 20°) and insoluble in it, but is miscible with alcohol, ether, and petrol. It readily dissolves fats, resins, sulphur, phosphorus and iodine.

The chemical properties of benzene are typical of aromatic hydrocarbons and are often called *aromatic properties*.. These include:

(i) **Resistance to oxidation.**—Benzene is a remarkably stable compound and resists oxidation by chromic acid or acid potassium permanganate.

(ii) **Halogenation,** the substitution of hydrogen by chlorine or bromine. Substitution takes place in presence of a catalyst (halogen carrier) such as iron powder or iodine. Halogenated products containing from one up to six atoms of halogen are obtained.

$$C_6H_6 + Cl_2 = C_6H_5Cl \text{ (monochloro benzene)} + HCl.$$

$$C_6H_5Cl + Cl_2 = C_6H_4Cl_2 \text{ (dichloro benzene)} + HCl, \text{ and so on.}$$

(iii) **Nitration,** the substitution of hydrogen by the nitro group, $-NO_2$. Benzene reacts with concentrated nitric acid in presence of strong sulphuric acid, forming nitrobenzene—the sulphuric acid absorbs the water formed in the process. Dilute nitric acid has no action upon benzene. $C_6H_6 + HO.NO_2 = C_6H_5.NO_2$ (nitrobenzene) $+ H_2O$.

(iv) **Sulphonation,** the substitution of hydrogen by the sulphonic acid group, $-SO_3H$. Concentrated sulphuric acid, on warming, dissolves benzene forming benzene sulphonic acid.

$$C_6H_6 + HO.SO_3H = C_6H_5.SO_3H \text{ (benzene sulphonic acid)} + H_2O.$$

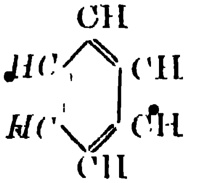
(v) **Friedel-Crafts reaction,** the introduction of an alkyl or acyl group into the benzene nucleus in presence of anhydrous aluminium chloride. The reaction is described under toluene.

$$C_6H_6 + C_2H_5Br = C_6H_5.C_2H_5 \text{ (ethyl benzene)} + \cancel{HCl}.\ HBr$$

$$C_6H_6 + CH_3COCl = C_6H_5.CO.CH_3 \text{ (phenyl methyl ketone)} + HCl.$$

Sulphonation, nitration, and Friedel-Crafts reaction distinguish aromatic hydrocarbons from the aliphatic.

Unlike the aliphatic compounds which are *open chain* compounds, the aromatic hydrocarbon benzene possesses a *closed chain* or *ring* of six carbon atoms. Benzene has a regular hexagon formula with alternate single and double bonds. The famous German chemist Kekule (1829-1896) suggested the hexagonal formula for benzene in 1865.



Benzene contains three double bonds in a closed ring, and forms additive compounds with hydrogen, chlorine and bromine.

(vi) In bright sunlight benzene reacts with chlorine or bromine, giving benzene hexachloride, $C_6H_6Cl_6$ or benzene hexabromide, $C_6H_6Br_6$. It is reduced to cyclohexane, C_6H_{12}, by hydrogen in presence of finely idvided nickel at 160°.

$$C_6H_6+3Cl_2 = C_6H_6Cl_6 ; C_6H_6+3H_2 = C_6H_{12}.$$

Benzene reacts with ozone, forming a triozonide, pointing to the presence of 3 double bonds in it.

$$C_6H_6+3O_3 = C_6H_6(O_3)_3 \text{ (benzene triozonide).}$$

(vii) *Failure to respond to the usual tests for unsaturation.*—In spite of 3 double bonds in benzene, it is very unlike the olefines, and in marked contrast *benzene reacts neither with bromine water nor with a solution of potassium permanganate in the cold*, the reagents which readily attack the olefines. Benzene also forms no addition compounds with halogen acids or strong sulphuric acid (*cf.* olefines, p 333). Benzene, therefore, possesses a peculiar degree of unsaturation.

Uses of benzene.—Benzene is used: (i) as a solvent for oils and fats, (ii) for dry cleaning, (iii) for motor fuel, and (iv) for making nitrobenzene, and the insecticide *gammexane*, $C_6H_6Cl_6$.

Benzene and its homologues.—Benzene is the starting point of a homologous series, C_nH_{2n-6}.

Benzene, C_6H_6 —C_6H_5 is monovalent phenyl group.
Toluene, methyl benzene, C_7H_8 or $C_6H_5.CH_3$.
Xylene, dimethyl benzene, C_8H_{10} or $C_6H_4.(CH_3)_2$.
Mesitylene, *sym*-trimethyl benzene, C_9H_{12} or $C_6H_3.(CH_3)_3$.

The monovalent radicals of the aromatic hydrocarbons, e.g., —C_6H_5, phenyl; —C_7H_7, tolyl, etc., are known as aryl radicals (*cf.* alkyl radicals)

Tolune, methyl benzene, phenyl methane, $C_6H_5.CH_3$ is the first homologue of benzene. Toluene received its name from *tolu balsam*, a resin, from which it is obtained by distillation. It is made from coal tar by fractional distillation. It also occurs in Assam and Borneo petroleum. Toluene can be synthesised by: (i) **Fittig's method** from bromobenzene and methyl iodide by the action of sodium in dry ether medium. $C_6H_5Br+CH_3I+2Na = C_6H_5.CH_3+NaBr+NaI$.

Sodium is added in thin slices to a mixture of bromobenzene and methyl iodide in dry ether solution, when the reaction begins spontaneously. After the reaction is over, the liquid is decanted from the sodium salts and toluene separated by distillation. The method recalls Wurtz synthesis of paraffins.

(ii) **Friedel-Crafts reaction** from benzene and methyl chloride in presence of anhydrous aluminium chloride which acts as a catalyst.

$$C_6H_6+CH_3Cl = C_6H_5.CH_3+HCl.$$

Anhydrous aluminium chloride is added to benzene and methyl chloride (a gas) is passed in, when hydrogen chloride rapidly evolves and toluene is formed. The product is poured into water and the upper layer of oil is removed and fractionated for toluene.

Synthesis of toluene from benzene shows it to be methyl benzene $C_6H_5.CH_3$. Higher homologues can be synthesised similarly.

$$C_6H_6+C_2H_5Br = C_6H_5.C_2H_5 \text{ (ethyl benzene)}+HCl.$$

Benzene reacts with acetyl chloride in presence of aluminium chloride to give phenyl methyl ketone, also called acetophenone (a hypnotic). $C_6H_6+CH_3COCl = C_6H_5.CO.CH_3$ (acetophenone)$+HCl$.

Aromatic hydrocarbons alone undergo Friedel-Crafts reaction. Neither the paraffins nor olefines share this property.

Nucleus and side chain.—The aromatic part or ring in a compound like toluene is known as **nucleus** and the aliphatic part is called a **side chain.** Toluene contains a nucleus (benzene ring) and a side chain (the methyl group, $-CH_3$). On oxidation the side chain is converted into a carboxyl group, $-COOH$, the nucleus remains intact. Thus, on oxidation with chromic acid or permanganate toluene yields benzoic acid.

$$C_6H_5.CH_3+3O = C_6H_5.COOH+H_2O$$

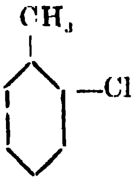
Any side chain such as ethyl, propyl, etc., containing several carbon atoms, give a carboxyl group, $-COOH$, on oxidation.

Properties of toluene.—Toluene is a colourless liquid with a benzene-like smell. It is lighter than water (sp. gr. 0.869 at 16°). It boils at 110° and freezes at −98°. It closely resembles benzene in properties.

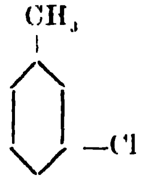
Action of chlorine on toluene.– Toluene like benzene, undergoes substitution by chlorine. Depending on conditions, substitution may take place in the nucleus or in the side chain:

(i) If chlorine is passed into **cold toluene** in presence of a halogen carrier, e.g., iron powder, iodine, etc., substitution takes place in the nucleus, forming *ortho-* and *para-* chlorotoluenes mainly.

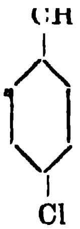
There are three isomeric monochlorotoluenes, the relative position of chlorine with respect to the $-CH_3$ group being different in each case. They are known as *ortho* (1 : 2), *meta* (1 : 3), and *para* (1 : 4), or in short, *o-*, *m-*, and *p-* respectively—the position of the CH_3 group in the nucleus is taken as 1.



o-chlorotoluene



m-chlorotoluene



p-chlorotoluene

(ii) If chlorine is passed into **boiling toluene** substitution takes place in the nucleus and the following products are formed successively:

Benzyl chloride, $C_6H_5.CH_2Cl$.
Benzal chloride or benzylidene chloride, $C_6H_5.CHCl_2$.
Benzo trichloride or benzenyl chloride, $C_6H_5.CCl_3$.

Uses of toluene.—Toluene is the starting material for making *saccaharin* (550 times sweeter than cane sugar), T.N.T. (trinitrotoluene), and many dyes and drugs. Toluene, like benzene, is a solvent and motor fuel.

XVI

HALOGEN COMPOUNDS

Aromatic halogen compounds.—The hydrogen atom on the ring of the aromatic hydrocarbons may be replaced by chlorine or bromine; the resulting compounds are *aryl halides* (*cf.* alkyl halides).

Chlorobenzene and bromobenzene.—They are made by passing *dry* chlorine (or adding bromine drop by drop) into benzene in presence of some iron powder until the requisite specific gravity of the product is reached. The product is purified by distillation. Iodobenzene is made by the action of iodine and boiling nitric acid on toluene.

$$2C_6H_6+2I+O(HNO_3) = 2C_6H_5I+H_2O.$$

The three aryl halides are colourless liquids and heavier than water in which they are insoluble. Chlorobenzene is used in making D.D.T. and synthetic phenol.

Chlorotoluene, $C_6H_4(CH_3)Cl$. It exists in three isomeric forms, the ortho-, meta-, and para- compounds. The o- and p- chlorotoluenes are made by direct chlorination of toluene in presence of a halogen carrier (p. 86). The chlorotolunes are colourless liquids, resembling chlorobenzene.

Benzyl chloride, benzal chloride and benzotrichloride.—They are made by chlorinating toluene in the side chain. Chlorine is passed into *boiling* toluene until the requisite specific gravity of the product is reached. The product is then separated by distillation.

$C_6H_5.CH_3+Cl_2 = C_6H_5.CH_2Cl$ (benzyl chloride, b.p. 176°)$+HCl$.
$C_6H_5.CH_3+2Cl_2 = C_6H_5.CHCl_2$ (benzal chloride, b.p. 206°)$+2HCl$.
$C_6H_5.CH_3+3Cl_2 = C_6H_5CCl_3$ (benzo trichloride, b.p. 213°)$+3HCl$.

They are colourless liquids, heavier than water, in which they are insoluble.

Properties of halogen derivatives.—Nuclear halogen compounds (aryl halides), e.g., chlorobenzene, chlorotoluene, have agreeable smell, but compounds with halogen substituted in the side chain, e.g., benzyl chloride, etc., have pungent smell and attack the eyes. In comparison with the alkyl halides, the aryl halides are very unreactive —the halogen is firmly attached to the nucleus. Thus, chlorobenzene is unaffected by such reagents as dilute acids or alkalis, moist silver oxide, alcoholic potash, alcoholic ammonia and potassium cyanide, which readily affect an alkyl halide. Aryl halide, however, reacts with mtallic sodium in ether medium (Fittig's method, p. 85).

$$C_6H_5Br+C_2H_5Br+2Na = C_6H_5.C_2H_5 \text{ (ethyl benzene)}+2NaBr.$$

But the side chain halogen compounds closely resembles alkyl halides. Thus, benzyl chloride readily reacts with aqueous alkali, alcoholic ammonia and potassium cyanide.

$C_6H_5CH_2Cl + NaOH = C_6H_5CH_2OH$ (benzyl alcohol) $+ 2NaCl$.
$C_6H_5CH_2Cl + 2NH_3 = C_6H_5CH_2NH_2$ (benzyl amine) $+ NH_4Cl$.
$C_6H_5CH_2Cl + KCN = C_6H_5CH_2CN$ (benzyl cyanide) $+ KCl$.

Benzal chloride on hydrolysis with aqueous alkali, e.g., milk of lime, gives benzaldehyde:

$$C_6H_5CHCl_2 + Ca(OH)_2 = C_6H_5CHO + CaCl_2 + H_2O.$$

Benzotrichloride on hydrolysis with milk of lime or steam under pressure gives benzoic acid: $C_6H_5CCl_3 + 2H_2O = C_6H_5COOH + 3HCl$.

Benzyl chloride, $C_6H_5CH_2Cl$, is isomeric with chlorotoluene, $C_6H_4(CH_3)Cl$. But on oxidation with alkaline permanganate chlorotoluene gives chlorobenzoic acid, $C_6H_4Cl.COOH$, whereas benzyl chloride gives benzoic acid, C_6H_5COOH. Hence oxidation offers a method to distinguish between nuclear and side chain chlorinated hydrocarbons.

$C_6H_5CH_2Cl + O_2 = C_6H_5COOH$ (benzoic acid) $+ HCl$.
$C_6H_4(CH_3)Cl + 3O = C_6H_4Cl.COOH$ (chlorobenzoic acid) $+ H_2O$.

XVII

* NITROBENZENE

Nitrobenzene, $C_6H_5NO_2$, is made by direct nitration of benzene with nitric acid; usually a mixture of concentrated nitric and sulphuric acids ('mixed acid') is used in introducing a nitro group, $-NO_2$, into the benzene nucleus. $C_6H_6 + HO.NO_2 = C_6H_5NO_2 + H_2O$.

A cold mixture of concentrated nitric acid of sp. gr. 1·45 (60 g.) and concentrated sulphuric acid (80 g.) is slowly run from a tap-funnel into well-cooled benzene taken in a flask, which is well shaken during the process—the temperature is kept at about 35—40° by cooling the flask in water. After all the acid has been added, the flask is heated for half an hour on a water bath—during this operation the flask is shaken frequently. The flask is then cooled and its contents poured into a large excess of water—nitrobenzene separates at the bottom as a heavy pale yellow oil. The oil is separated by a tap-funnel, washed with water, then with dilute sodium carbonate solution until free from acid, and finally with water once more. The nitrobenzene is then run off and dried over anhydrous calcium chloride until it becomes clear. The oil is then filtered into a distilling flask and distilled, using an air condenser—the distillate collected between 205—210° is fairly pure nitrobenzene.

Properties and uses.—Nitrobenzene is a pale yellow oil (b.p. 205°) of sp. gr. 1·2 at 20°. It is insoluble in water and is poisonous. It has a pleasant smell like that of bitter almonds for which it is often substituted in perfumes under the name of *oil or essence of mirbane*. It is also used in scenting soaps and polishes. But its chief use is in making aniline and benzidine. In strongly acid solution it is reduced to aniline by nascent hydrogen—suitable reducing agents are iron filings, granulated tin or zinc, with strong hydrochloric or glacial acetic acids.

$$C_6H_5NO_2 + 6H = C_6H_5.NH_2 \text{ (aniline)} + 2H_2O.$$

XVIII

ANILINE

Aniline, aminobenzene, phenylamine, $C_6H_5NH_2$.—Aniline was first obtained in 1826 by distillation of indigo from India. The Portuguese name for indigo (Sanskrit *nil* is dark blue or indigo plant) is *anil*, and hence the name *aniline*. Aniline occurs in small quantities in coal tar and bone oil.

In the laboratory aniline is prepared by reducing nitrobenzene with tin and concentrated hydrochloric acid.

$$C_6H_5NO_2+6H = C_6H_5NH_2 \text{ (aniline)}+2H_2O$$
$$C_6H_5NH_2+HCl = C_6H_5NH_2.HCl \text{ (aniline hydrochloride)}$$

Nitrobenzene (25 g.) and granulated tin (50 g.) are taken in round-bottom flask fitted with an air condenser and concentrated hydrochloric acid (100 c.c.) is added in small amounts (5 10 c.c.) at a time with shaking. Much heat is evolved and hence the flask is cooled in water to prevent the reaction-mixture from boiling. When all the acid is added (in course of half an hour), the flask is heated on a water bath until smell of nitrobenzene has disappeared (about one hour). Tin reacts with hydrochloric acid, giving nascent hydrogen which reduces nitrobenzene to aniline. Aniline, being a base, combines with hydrochloric acid forming aniline hydrochloride

After the reduction is complete, the flask is cooled and an excess of strong caustic soda solution (50 gm. in 100 c.c.) added until the liquid is alkaline to liberate aniline from its salt—the liberated aniline floats on the surface as a dark oil and is separated by *distillation in steam.*

Steam from the can B is passed into the flask F containing the liberated aniline. The flask (fitted with a condenser and receiver) is placed in a sloping position and heated on a sand tray (fig. 7). Aniline is volatile in steam. The steam carries with it the vapour of aniline which is condensed and collected with the water in the receiver. The aniline in the receiver is then separated by shaking in a tap-funnel with ether, which dissolves the aniline. The ether layer is then dried over anhydrous solid caustic potash, and then decanted into a dry flask. The ether is distilled off on waterbath, and then the aniline is distilled over the flame, using an air condenser and the distillate between 182-185° collected. Aniline boils at 182-183°.

Steam distillation. —The boiling point of two *immiscible* liquids (liquids which do not dissolve into one another) is determined by their combined vapour pressures. When this is equal to the atmospheric pressure, the mixture boils and both liquids distil. The distillation

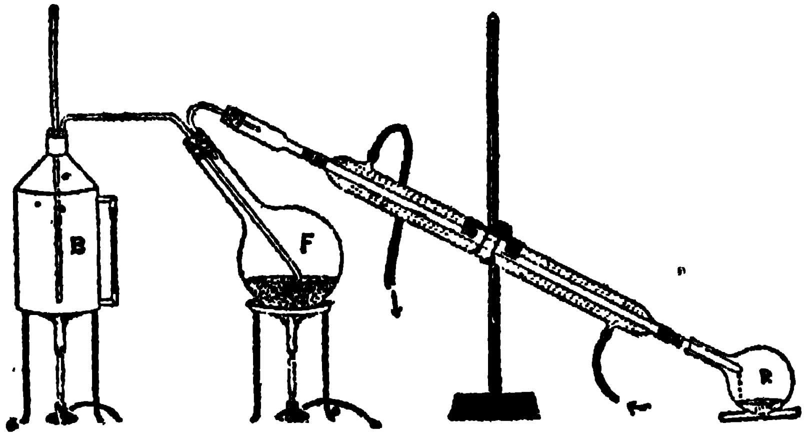


Fig. 7

takes place at a temperature which is below the normal boiling point of water, i.e. below 100°. This is the principle of steam distillation. At about 98·5° the sum of the vapour pressures of aniline and water equals the atmospheric pressure, and the mixture boils, and therefore, aniline distils in steam much below its own boiling point.

Organic liquids which are volatile with steam but are immiscible with water, can be purified by steam distillation. The process is useful in purifying organic substances which are likely to decompose when heated to their normal boiling points, e.g., glycerine. Steam distillation is of practical value in separating an organic substance from non-volatile impurities. Rose oil is separated from rose petals by steam distillation.

Commercially, aniline is made by reducing nitrobenzene with iron filings, water and some hydrochloric acid, instead of (very expensive) tin. The aniline is liberated from its salt, aniline hydrochloride, by cheaper milk of lime, and then steam distilled.

Aniline is also made technically by reacting chlorobenzene with aqueous ammonia under high pressure at 200° in presence of cuprous oxide and chloride.

$$2C_6H_5Cl+2NH_3+Cu_2O = 2C_6H_5NH_2+Cu_2Cl_2+H_2O.$$

Aniline can also be made by electrolytic reduction of nitrobenzene in a mixture of sulphuric acid and alcohol.

Properties of aniline.—(i) Aniline (b.p. 183°) is an oily liquid (sp. gr. 1·024 at 16°) with a characteristic smell ; it is colourless, when freshly distilled, but readily darkens on exposure to light and air. It is very sparingly soluble in water and dissolves readily in alcohol and ether. It is poisonous.

(ii) *It is a very weak base* (weaker than aliphatic amines, e.g., $C_2H_5NH_2$, and ammonia) and forms salts with acids, e.g., aniline hydrochloride, $C_6H_5NH_2.HCl$, aniline sulphate, $(C_6H_5NH_2)_2.H_2SO_4$, —the salts are soluble in water but the solution gives acid reaction due to hydrolysis. $C_6H_5NH_2.HCl \rightleftharpoons C_6H_5NH_2+HCl$.

(iii) Carbylamine reaction.—Aniline is a primary aromatic amine, and like aliphatic primary amines, it gives carbylamine reaction when warmed with chloroform and alcoholic potash—phenyl isocyanide, C_6H_5NC of intolerable smell being formed.

$$C_6H_5NH_2+CHCl_3+3KOH = C_6H_5NC+3KCl+3H_2O.$$

(iv) Acetylation.—Aniline (like an aliphatic primary amine) undergoes acetylation, i.e., the acetyl group, CH_3CO-, replaces one of the hydrogen atoms in the amino group, when treated with acetyl chloride, acetic anhydride, or even glacial acetic acid, yielding acetanilide, $C_6H_5NH.COCH_3$.

$$C_6H_5NH_2+ClCOCH_3 = C_6H_5NH.COCH_3+HCl.$$

(v) Methylation.—Aniline, like aliphatic amines, undergoes methylation when heated with methyl iodide under a reflux condenser, yielding methyl- and dimethyl aniline.

$C_6H_5.NH_2 + CH_3I = C_6H_5NHCH_3$ (methyl aniline) + HI

$C_6H_5.NHCH_3 + CH_3I = C_6H_5N(CH_3)_2$ (dimethyl aniline) + HI

✓ **(vi) Diazotisation.**—In acid solution aniline (e.g., a solution of aniline hydrochloride in dilute hydrochloric acid) reacts with nitrous acid *in the cold*, forming benzene diazonium salt. This is known as *diazo reaction.* On warming the resulting solution, the diazonium salt is decomposed by water, yielding phenol.

$$\begin{array}{l} C_6H_5.NH_2.HCl \\ +\ NO.OH = C_6H_5N_2Cl + 2H_2O \end{array}$$

Benzene diazonium chloride

$$C_6H_5N_2Cl + H.OH = C_6H_5OH \text{ (phenol) } + N_2 + HCl$$

A primary aromatic amine such as aniline alone gives the diazo reaction. An aliphatic primary amine does not give diazo reaction but forms alcohol, nitrogen and water when treated with nitrous acid.

$$C_2H_5NH_2 + NO.OH = C_2H_5OH + N_2 + H_2O.$$

(vii) **Sulphonation.**—When treated with fuming sulphuric acid at 180° aniline forms aniline-p-sulphonic acid or sulphanilic acid, $C_6H_4(NH_2).SO_3H$, used in making dyes, e.g., methyl orange.

$$C_6H_5.NH_2 + HO.SO_3H = C_6H_4.(NH_2).SO_3H + H_2O.$$

Aniline sulphate on heating at 200° also gives sulphanilic acid:

$$C_6H_5NH_2.H_2SO_4 = p\text{-}NH_2\text{-}C_6H_4\text{-}SO_3H + H_2O$$

(xiii) **Bromination.**—Aniline readily reacts with bromine water, giving a white precipitate of 2-4-6 tribromo aniline, $C_6H_2Br_3.NH_2$. Chlorine reacts similarly, giving 2-4-6 trichloro aniline.

$$C_6H_5.NH_2 + 3\,Br_2 = C_6H_2Br_3.NH_2 + HBr.$$

(ix) **Nitration.**—Aniline is readily oxidised by concentrated nitric acid (the amino group being destroyed), and hence to effect nitration the amino group is first '*protected*' *by acetylation* by boiling with glacial acetic acid when acetanilide, $C_6H_5NH.COCH_3$, is formed.

The acetanilide, on nitration with fuming nitric acid in the cold, gives o- and p- nitro acetanilides. These compounds on hydrolysis (by boiling with strong hydrochloric acid) yield o-nitro aniline and p-nitro aniline.

$$C_6H_5.NH.COCH_3 + HO.NO_2 = NO_2.C_6H_4.NHCOCH_3 + H_2O$$
$$NO_2C_6H_4.NH.COCH_3 + H.OH = NO_2.C_6H_4.NH_2 + CH_3COOH.$$

(x) Aniline is very sensitive to oxidising agents. A solution of potassium dichromate acidified with dilute sulphuric acid oxidises aniline to *aniline black*, an important dye

Uses of aniline.—Aniline is used in making indigo, many aniline dyes, and drugs, e.g., atoxyl and antifebrin.

Tests for aniline.—(i) Aniline gives carbylamine reaction.

(ii) It gives an intense violet colour with a solution of bleaching powder or sodium hypochlorite.

(iii) Aniline (e.g., an aqueous solution of aniline hydrochloride) gives a white precipitate of tribromo aniline with bromine water.

(iv) **Aniline gives diazo reaction.** A cold solution of sodium nitrite is added to an *ice-cold* solution of aniline hydrochloride in dilute hydrochloric acid, when the solution turns yellow and contains benzene diazonium chloride. On pouring this solution into (i) a solution of phenol in causic soda, a deep orange red colour develops, or (ii) a solution of beta-naphthol in caustic soda, a scarlet precipitate is formed. The diazo reaction identifies a primary aromatic amine.

Acetanilide, phenyl acetamide, antifebrin, $C_5H_5NH.COCH_3$.—It is prepared by acetylation of aniline (p. 90).

A mixture of freshly distilled aniline (10 c.c.) with glacial acetic acid (10 c.c.) and actyl chloride (10 c.c.) is gently boiled for about an hour in a flask fitted with a long glass tube (to condense the acetic acid vapour which is given off) ; the contents of the flask is then poured into water, when acetanilide is precipitated as a crystalline mass. This is filtered and re-crystalised from water.

$$C_5H_5NH_2+CH_3COOH = C_6H_5NH.COCH_3+H_2O,$$

Acetanilide is a colourless crystalline solid, m.p. 114°. It is sparingly soluble in cold water but readily in hot water. It is hydrolysed into aniline and acetic acid by boiling with strong hydrochloric acid. The reaction recalls the comparable behaviour of acetamide (p. 51).

$$C_6H_5NH.COCH_3 + HOH = C_6H_5NH_2 + CH_3COOH.$$

Acetanilide is used in medicine as a febrifuge (to reduce the body temperature) under the name of antifebrin.

The diazo reaction.—The diazo reaction was discovered by P. Griess, a German chemist, in 1860, and is very useful in organic synthesis and in making the synthetic dye-stuffs, known as *azo-dyes* Aromatic primary amines such as aniline give diazo reaction (p. 90 and 91), and the process is known as **diazotisation.**

Several important reactions of a diazo salt i.e., benzene diazonium chloride, are mentioned below:

(i) On boiling an aqueous solution of the diazo salt nitrogen evolves and phenol is formed.

$$C_6H_5N_2Cl+H.OH = C_6H_5OH + N_2+HCl.$$

(ii) When the diazo salt is reduced with a solution of sodium stannite, benzene is formed. The reduction may also be done by boiling with alcohol.

$$C_6H_5N_2Cl+NaOH+Na_2SnO_2 = C_6H_6+N_2+Na_2SnO_3+NaCl$$

$$C_6H_5N_2Cl+CH_3CH_2OH = C_6H_6+N_2+CH_3CHO+HCl$$

(iii) When the diazonium salt is warmed with potassium iodide solution iodobenzene is formed. $C_6H_5N_2Cl+KI = C_6H_5I+N_2+KCl$.

(iv) **Sandmeyer reaction.** —When a solution of the diazonium salt is treated with: (a) a solution of cuprous chloride in hydrochloric acid, (b) a solution of cuprous bromide in hydrobromic acid, (c) a solution of cuprous cyanide in potassium cyanide, chlorobenzene, bromobenzene, and cyanobenzene (phenyl cyanide) are formed respectively.

$$C_6H_5N_2Cl + [CuCl] = C_6H_5Cl + N_2 + [CuCl]$$

$$C_6H_5N_2Cl + CuBr = C_6H_5Br + N_2 + CuCl$$

$$C_6H_5N_2Cl + CuCN = C_6H_5CN + N_2 + CuCN.$$

Thus, via the formation of a diazo salt the amino group, -NH$_2$, in aniline may be replaced by H, OH, Cl, Br, I and CN.

(v) When reduced with stannous chloride and hydrochloric acid, benzene diazonium chloride yields phenyl hydrazine, $C_6H_5NH.NH_2$.

$$C_6H_5N = NCl+2SnCl_2+3HCl = C_6H_5NH.NH_2+2SnCl_4.$$

XIX

PHENOLS

Phenol, carbolic acid, C_6H_5OH.—Phenol is hydroxy benzene, in which a hydrogen atom of the nucleus is replaced by hydroxyl. Structurally, it is apparently analogous to an aliphatic alcohol, e.g., CH_3OH and C_2H_5OH. But unlike the latter, *phenol is a weak acid*, although it possesses some properties of alcohols. But an aromatic alcohol like benzyl alcohol, $C_6H_5CH_2OH$, which contains a hydroxyl group in the side chain, is the real analogue of an aliphatic alcohol and possesses the properties of true alcohols.

Source of phenol.—The main source of phenol is coal tar. The middle oil fraction of coal tar contains phenol together with some naphthalene. On cooling naphthalene mostly deposits and is separated by centrifuging. The liquid is then treated with caustic soda solution to dissolve the phenol as sodium phenate. The alkaline liquid is separated from any undissolved oil, and then acidified with sulphuric acid (or carbon dioxide is passed into liquid) when phenol separates on the surface as a dark-coloured oil. The oil is removed and distilled—the distillate is almost pure phenol. 1 ton of coal gives about 1·5 lb. of phenol.

$$C_6H_5OH + NaOH = C_6H_5ONa \text{ (sodium phenate)} + H_2O$$

$$C_6H_5ONa + H_2SO_4 = C_6H_5OH + NaHSO_4.$$

Synthetic phenol is made technically from benzene by two methods: (i) Sodium benzene sulphonate is fused with caustic soda at 350° to give sodium phenate. The sodium phenate is dissolved in water and the solution treated with sulphuric acid or carbon dioxide under pressure to liberate phenol, which is then separated by distillation.

$$C_6H_5SO_3Na + 2NaOH = C_6H_5ONa + Na_2SO_3 + H_2O$$

$$C_6H_5ONa + H_2O + CO_2 = C_6H_5OH + NaHCO_3$$

Benzene on sulphonation by heating with concentrated sulphuric acid, yields benzene sulphonic acid.

$$C_6H_6 + HO.SO_3H = C_6H_5.SO_3H + H_2O.$$

(ii) Chlorobenze is heated with a 10 per cent caustic soda solution at 320° under a pressure of 200 atmospheres in copper tubes, when sodium phenate is formed. Copper acts as a catalyst in the process.

$$C_6H_5Cl + 2NaOH = C_6H_5ONa + NaCl + H_2O.$$

The phenol is then liberated by acid or carbon dioxide. Benzene is converted to chlorobenzene by direct chlorination (p. 87).

In a recent method chlorobenzene is catalytically hydrolysed with steam at 425° to phenol, and the regenerated HCl is used in presence of air and a catalyst to chorobenzene which again goes through the process. $C_6H_5Cl + H.OH = C_6H_5OH + HCl$

$$C_6H_6 + HCl + O \text{ (air)} = C_6H_5Cl + H_2O$$

Benzene diazonium chloride on hydrolysis with water gives phenol (p. 92), but this is not a technical method.

Properties of Phenol. —(i) Phenol forms large, colourless, deliquescent crystals which melt at 42° and boil at 183°. It turns pink on exposure to light and air. It has a characteristic smell, is highly poisonous and has a strongly corrosive action on the skin, quickly causing blisters. It possesses antiseptic properties. It is freely soluble in alcohol and ether, but is moderately soluble (1 part in 15) in cold water ; above 68° phenol is freely soluble in water. Phenol is volatile in steam.

(ii) Phenol is a very weak acid, (even weaker than carbonic acid) and readily dissolves in caustic soda (or potash), forming salts, called *phenates* or *phenoxides*. *Sodium carbonate, however, has no action upon phenol.* An aqueous solution of phenate is strongly alkaline to litmus due to hydrolysis: $C_6H_5ONa + HOH \rightleftharpoons C_6H_5OH + NaOH$.

A phenate is decomposed by acid—even a feeble acid like carbonic acid decomposes it—liberating phenol.

$$C_6H_5ONa + H_2O + CO_2 = C_6H_5OH + NaHCO_3.$$

The decomposition of phenates by carbon dioxide is utilised in separating phenol from acids such as benzoic acid, salicylic acid, etc., whose sodium salt is not acted on by carbon dioxide. A mixture of phenol and benzoic acid (or salicylic acid) is neutralised with caustic soda, forming sodium phenate and benzoate (or salicylate). On passing carbon dioxide through the solution, phenol is set free and is extracted with ether. The ether is removed on warming the ether extract on water bath—the residual oily liquid is phenol. The alkaline solution which contains the benzoate (or salicylate) on acidification with hydrochloric acid, precipitates benzoic (or salicylic) acid.

(iii) Phenol shows alcoholic properties in forming esters and ethers. When heated with acetyl chloride or acetic anhydride, phenol gives acetate, $C_6H_5O.COCH_3$: $C_6H_5OH + ClCOCH_3 = C_6H_5O.CO.CH_3 + HCl$.

With benzoyl chloride in presence of caustic soda solution, phenol gives phenyl benzoate $C_6H_5O.CO.C_6H_5$ **(Schotten-Baumann reaction).**

$$C_6H_5OH + ClCOC_6H_5 = C_6H_5O.COC_6H_5 + HCl.$$

Sodium phenate reacts with alkyl halides on heating, giving phenol ethers (*Williamson synthesis*).

$$C_6H_5ONa + ICH_3 = C_6H_5OCH_3 \text{ (anisole)} + NaI.$$
$$C_6H_5ONa + IC_2H_5 = C_6H_5OC_2H_5 \text{ (phenetole)} + NaI.$$

Anisole (phenyl methyl ether) and phenetole (phenyl ethyl ether) are fragrant smelling liquids.

Phenol reacts with phosphorus pentachloride, giving chlorobenzene.

$$C_6H_5OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl.$$

(iv) Phenol readily undergoes sulphonation and nitration, yielding phenol sulphonic acid and nitrophenol, and hence in its reaction with sulphuric and nitric acids phenol acts as an aromatic compound and *not as an alcohol.* Nitration can be done by dilute nitric acid.

$$C_6H_5OH + HO.SO_3H = (OH).C_6H_4.SO_3H + H_2O$$
$$C_6H_5OH + HO.NO_2 = (OH).C_6H_4.NO_2 + H_2O.$$

Picric acid is 2-4-6 trinitrophenol, $C_6H_2(OH)(NO_2)_3$, an explosive.

(v) Phenol is reduced to benzene, on distillation with zinc dust.

$$C_6H_5OH + Zn = C_6H_6 + ZnO.$$

(vi) Aniline is obtained by heating phenol with a compound of zinc chloride and ammonia.

$$C_6H_5OH + ZnCl_2.NH_3 = C_6H_5NH_2 + ZnCl_2 + H_2O.$$

(vii) With bromine water, phenol readily and quantitatively gives a white precipitate of 2-4-6 tribromophenol.

$$C_6H_5OH + 3Br_2 = C_6H_2(OH)Br_3 + 3HBr.$$

Tests.—(i) An aqueous solution of phenol gives (a) a violet colour with ferric chloride solution and (b) a white precipitate with bromine water.

(ii) Phenol gives **Liebermann's reaction.** Phenol is gently warmed and a minute crystal of sodium nitrite and 2 or 3 drops of concentrated sulphuric acid added to it—the solution turns brown which quickly changes to blue. On pouring in water, it turns red, but is turns blue again, on adding caustic soda.

Uses.—(i) Phenol is a powerful antiseptic, disinfectant and a germicide, and hence its use in dilute solution (3 per cent) in dressing and washing wounds, and for disinfecting surgical instruments, rooms, etc.

The common disinfectants (trade names '*phenyl*', *lysol*, etc.) are but mixtures of *cresols* (cresols, $C_6H_4.(CH_3).OH$, are phenols which are also present in coal tar) and soap solution.

(ii) Phenol is used in making plastics, e.g., bakelite, explosives, e.g., picric acid, developers, e.g., metol, dyes, e.g., phenophthalein, synthetic fibre, e.g., nylon, drugs, e.g., aspirin, salicylic acid and salol (antiseptic). Bakelite is made by condensing phenol and formaldehyde in presence of ammonia.

Di- and trihydric phenols.—Ordinary phenol is monohydroxy benzene and is called monohydric phenol, but if more than one hydrogen atom in the benzene nucleus is replaced by hydroxyl group, the di- and tri hydric phenols, etc., are obtained.

There are three isomeric dihydric phenols :

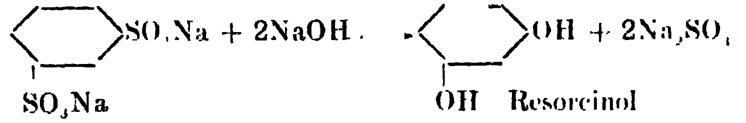
Catechol, 1 : 2 dihydroxy benzene, $C_6H_4(OH)_2$, m.p. 104°

Resorcinol, 1 : 3 dihydroxy benzene, $C_6H_4(OH)_2$, m.p. 119°.

Quinol, 1 : 4 dihydroxy benzene, $C_6H_4(OH)_2$, m.p. 169°

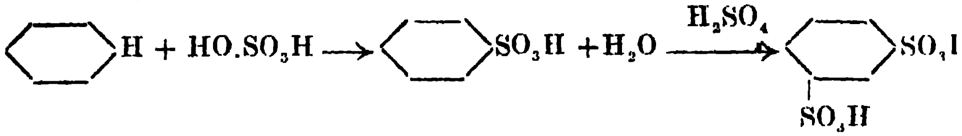
Quinol is also called hydroquinone.

Resorcinol, 1 : 3 dihydroxy benzene, $C_6H_4(OH)_2$, is a colourless crystalline solid (m.p. 119°, which is readily soluble in water, alcohol, and ether. Its reactions resemble those of phenol. Thus it gives a deep violet colour with ferric chloride solution, and a precipitate of tribromo resorcinol with bromine. It reduces Fehling's solution and also ammoniacal silver nitrate, but it is not as powerful a reducing agent as catechol and is of no value as a developer. It is mainly used in the preparation of the fluorescein and eosin dyes. Resorcinol is made by fusing sodium salt of m-benzene-disulphonic acid with caustic soda.



Therefore, resorcinol is m-dihydroxybenzene.

Benzene on sulphonation (p. 84) first gives benzene sulphonic acid, and then m-benzene disulphonic acid :



Pyrogallol, pyrogallic acid, $C_6H_3(OH)_3$, is a trihydric phenol. It is 1 : 2 : 3 trihydroxy benzene. Its alkaline solution readily absorbs oxygen and darkens in colour. Pyrogallol is a reducing agent and a photographic developer.

Cresols, cresylic acids, hydroxy toluene, $C_6H_4(CH_3)OH$.—The three isomers —o-, m- and p- cresol—are found in coal tar. The creosote oil fraction of coal tar contains them. In mixture with oil or soap, the creosote oil is used in making disinfecting liquids, e.g., *phenyle, lysol.*

* ALCOHOLS, ALDEHYDE AND ACIDS

Benzyl alcohol, $C_6H_5CH_2OH$.—It is a true aromatic alcohol in which the OH group is in the side chain (Phenol contains OH- group in the benzene nucleus). It occurs in jasmine oil, and in tolu and peru balsams, either in free state or as an ester.

Benzyl alcohol is obtained by: (i) reducing benzaldehyde with sodium amalgam and water.

$$C_6H_5CHO \text{ (benzaldehyde)} + 2H = C_6H_5CH_2OH.$$

(ii) hydrolysis of benzyl chloride by boiling with sodium carbonate solution.

$$2C_6H_5CH_2Cl + Na_2CO_3 + H_2O = 2C_6H_5CH_2OH + 2NaCl + CO_2.$$

(iii) boiling benzaldehyde with strong caustic soda solution, when benzyl alcohol and sodium benzoate are formed. This reaction is characteristic of an aromatic aldehyde and is known as **Cannizzarro's reaction.**

$$2C_6H_5CHO + NaOH = C_6H_5CH_2OH + C_6H_5COONa.$$

The benzyl alcohol is extracted with ether.

Properties. Benzyl alcohol is a colourless, *neutral* liquid (b.p. 206°), with a sweet aroma. It is freely soluble in alcohol and ether, but only moderately soluble in water.

It is a primary alcohol and closely resembles methyl or ethyl alcohol in chemical properties in reactions with Na, PCl_5, acids (in forming esters), oxidising agent, etc. Dilute nitric acid oxidises it to benzaldehyde and finally to benzoic acid.

$$2C_6H_5CH_2OH + 2Na = 2C_6H_5CH_2ONa \text{ (sodium benzylate)} + H_2$$
$$C_6H_5CH_2OH + PCl_5 = C_6H_5CH_2Cl \text{ (benzyl chloride)} + POCl_3 + HCl$$
$$C_6H_5CH_2OH + CH_3COCl = C_6H_5CH_2O.COCH_3 \text{ (benzyl acetate)} + HCl$$
$$C_6H_5CH_2OH + O = C_6H_5CHO \text{ (benzaldehyde)} + H_2O$$
$$C_6H_5CHO + O = C_6H_5COOH \text{ (benzoic acid).}$$

Benzaldehyde, oil of bitter almonds, C_6H_5CHO. Benzaldehyde may be made (i) in the laboratory by boiling benzyl chloride with copper nitrate solution; benzyl chloride is hydrolysed to benzyl alcohol which is then oxidised to benzaldehyde.

$$C_6H_5CH_2Cl + H.OH = C_6H_5CH_2OH + HCl.$$
$$C_6H_5CH_2OH + O = C_6H_5CHO + H_2O.$$

The product is distilled in steam, and benzaldehyde is extracted from the distillate by ether.

(ii) by distilling a mixture of calcium benzoate and calcium formate

$$\begin{matrix} C_6H_5COOCa' \\ + HCOOCa' \end{matrix} = C_6H_5CHO + CaCO_3$$

(iii) by partial oxidation of toluene by means of chromyl chloride, CrO_2Cl_2 **(Etard's reaction).** $C_6H_5CH_3 + 2O = C_6H_5CHO + H_2O$.

(iv) Commercially, by hydrolysis of benzal chloride by heating with milk of lime under pressure.

$$C_6H_5CHCl_2 + Ca(OH)_2 = C_6H_5CHO + CaCl_2 + H_2O.$$

or by partial oxidation of toluene with manganese dioxide and 65% sulphuric acid at 40°.

It occurs in bitter almonds as *amygdalin* which on hydrolysis with the enzyme *emulsion* (also present in bitter almonds) or hot dilute acids gives benzaldehyde, and hence the name oil of bitter almonds.

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + 2H_2O = C_6H_5CHO + \underset{\text{Glucose}}{2C_6H_{12}O_6} + HCN$$

Properties. —(i) Benzaldehyde is a colourless oily liquid (b.p. 179° and sp. gr. 1·05 at 15°) having the sweet aroma of bitter almonds. It is slightly soluble in water, but is miscible with alcohol and ether. It is volatile in steam.

(ii) It resembles acetaldehyde, CH_3CHO, in the following respecst:

(a) on oxidation, either by oxidising agents or by mere exposure to air, it gives benzoic acid.

(b) on reduction with sodium amalgam, it gives benzyl alcohol.

(c) it reacts with PCl_5, giving benzal chloride, $C_6H_5CHCl_2$.

(d) it forms cyanhydrin with HCN; and a bisulphite addition product with $NaHSO_3$.

(e) it reacts with NH_2OH, $NH_2.NH_2$ and $NH_2NHC_6H_5$, giving oxime, hydrazone and phenyl hydrazone respectively.

(f) It slowly reduces ammoniacal silver nitrate and Fehling's solution, and *slowly* restores the colour of Schiff's reagent.

But benzaldehyde **differs** from acetaldehyde in the following respects: (i) on heating with strong caustic soda (*or* potash), benzaldehyde gives benzyl alcohol and benzoate **(Cannizzarro's reaction).**

$$2C_6H_5CHO + NaOH = C_6H_5CH_2OH + C_6H_5COONa.$$

(ii) with ammonia at ordinary temperature, it gives hydrobenzamide, $(C_6H_5CH)_3N_2$: $3C_6H_5CHO + 2NH_3 = (C_6H_5CH)_3N_2 + 3H_2O$.

(iii) on heating with potassium cyanide in aqueous alcohol, it gives benzoin: $2C_6H_5CHO \longrightarrow C_6H_5CH(OH).CO.C_6H_5$ (benzoin).

(iv) It does not polymerise or undergo aldol condensation (p. 38) in presence of acid or alkalis.

Uses. - Benzaldehyde is used as a flavouring agent and in making dyes, e.g., malachite green

Benzoic acid, C_6H_5COOH. – It occurs in gum benzoin (a natural resin) from which it may be obtained by sublimation. It is present in horse's urine (about 2%) as *hippuric acid* (benzoyl glycine), $C_6H_5CO.NH.CH_2COOH$

Preparation.—Benzoic acid can be made: (i) by oxidation of an aromatic compound having a side chain in the benzene nucleus, e.g, toluene, $C_6H_5.CH_3$, benzyl chloride, $C_6H_5CH_2Cl$ etc. Oxidation is facilitated if the side chain is substituted; thus, $C_6H_5CH_2Cl$ is more readily oxidised than toluene itself.

Benzoic acid is made in the laboratory by oxidising benzyl chloride by heating with an alkaline solution of potassium permanganate. Manganese dioxide is precipitated during the process and the benzoic acid formed remains in solution as benzoate. On passing sulphurous acid, manganese dioxide dissolves and benzoic acid precipitates. $4KMnO_4 + 2H_2O = 4KOH + 4MnO_2$ (precipitated) $+ 6,O$

$$3C_6H_5CH_2Cl + 6,O = 3C_6H_5COOH + 3HCl.$$

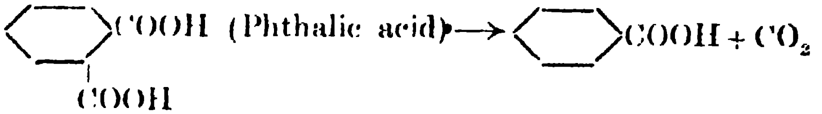
(ii) by hydrolysis of phenyl cyanide by boiling with strong sulphuric acid: $C_6H_5CN + 2H_2O \rightleftharpoons C_6H_5COOH + NH_3$

Benzoic acid is made commercially: (a) by hydrolysis of benzotrichloride by heating with milk of lime; benzoic acid precipitates on acidification with hydrochloric acid.

$$2C_6H_5CCl_3 + 4Ca(OH)_2 = (C_6H_5COO)_2Ca + 3CaCl_2 + 4H_2O$$

$$(C_6H_5COO)_2Ca + 2HCl = 2C_6H_5COOH + CaCl_2$$

(b) by passing the vapour of phthalic acid with excess of steam over heated zinc oxide (catalyst) at 450°, when CO_2 is eliminated.



Phthalic acid is made from naphthalene.

Properties. -(i) Benzoic acid forms colourless needles (m.p. 122°) which sublime on heating—the vapour having irritating action on throat, causing coughing and sneezing. It is volatile in steam. It is sparingly soluble in cold water, but readily dissolves in hot water, alcohol and ether.

(ii) Benzoic acid closely resembles acetic acid in properties which are determined by—COOH group, and gives corresponding derivatives, prepared in a similar way, namely:

Sodium benzoate, C_6H_5COONa
Benzoly chloride, C_6H_5COCl
Phenyl cyanide, C_6H_5CN

Ethyl benzoate, $C_6H_5COOC_2H_5$
Benzoic anhydride, $(C_6H_5CO)_2O$
Benzamide, $C_6H_5CONH_2$

These compounds possess the general character of the corresponding aliphatic compound.

Tests.—(i) A neutral solution of a benzoate gives a buff-coloured precipitate with ferric chloride solution.

(ii) A solution of benzoate on acidification with cold sulphuric acid, gives a white precipitate of benzoic acid.

(iii) When heated with soda lime, benzoic acid or a benzoate yields benzene:

$$C_6H_5COOH = C_6H_6 + CO_2.$$

Benzoyl chloride, C_6H_5COCl, is a colourless fuming liquid (b.p. 197°) of most irritating odour. It is made by the action of PCl_5 on benzoic acid: $C_6H_5COOH + PCl_5 = C_6H_5COCl + POCl_3 + HCl$

It is used in *benzoylation* of hydroxy or amino compounds—the benzoyl radical, C_6H_5CO—, replaces a hydrogen atom of the hydroxyl or the amino group, giving benzoyl derivatives. This is known as *Schothen-Baumann reaction*

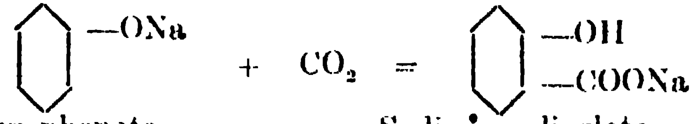
Benzoylation is done by shaking the compound with benzoyl chloride in presence of dilute (10 per cent) caustic soda solution, and then pouring in water, when the benzoyl derivatives separate. The benzoyl derivatives are usually solids which help in the identification of the hydroxy or the amino compound. On benzoylation, phenol gives phenyl benzoate, $C_6H_5COOC_6H_5$, m.p. 71° and aniline gives benzanilide, $C_6H_5CO.NHC_6H_5$, m.p. 163°.

$$C_6H_5COCl + HOC_6H_5 = C_6H_5COOC_6H_5 + HCl$$

$$C_6H_5COCl + NH_2.C_6H_5 = C_6H_5CO.NHC_6H_5 + HCl.$$

Salicylic acid, o-hydroxy benzoic acid, $C_6H_4(OH)COOH$.—It occurs naturally in blossoms of meadow sweet and as methyl salicylate in oil of winter green. It was first isolated from *salicin* (found in willow bark) and hence the name salicylic acid.

It is made synthetically from phenol by **Kolbe's reaction.** Dry sodium phenate is heated to 130° with carbondioxide in an autoclave under a pressure of 1·5 atmospheres for some hours, when sodium salicylate is formed. The product is dissolved in water and salicylic acid is precipitated from the solution by acidification with hydrochloric acid.



Sodium phenate Sodium salicylate

Properties.—(i) Salicylic acid forms colourless needles (m.p. 155°), sparingly soluble in cold water, but readily in hot water, alcohol and ether. Its vapour has irritating effect on throat.

(ii) It is a phenolic acid and gives the properties of hydroxyl and carboxyl groups linked to the nucleus, i.e., it gives reactions of both phenol, C_6H_5OH, and benzoic acid, C_6H_5COOH.

(iii) When heated with zinc dust, it gives benzoic acid, but on heating with soda lime it gives phenol.

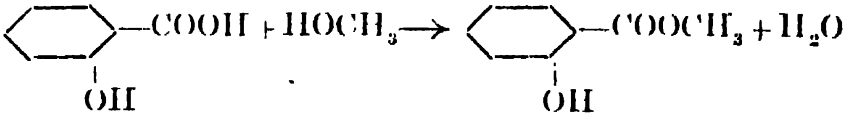
$$C_6H_4(OH)COOH + Zn = C_6H_5COOH + ZnO$$
$$C_6H_4(OH)COOH + NaOH = C_6H_5OH + NaHCO_3$$

(iv) It dissolves in sodium carbonate solution, forming sodium salicylate—sodium carbonate has no action upon phenolic —OH group

$$2C_6H_4(OH)COOH + Na_2CO_3 = 2C_6H_4(OH)COONa + H_2O + CO_2$$

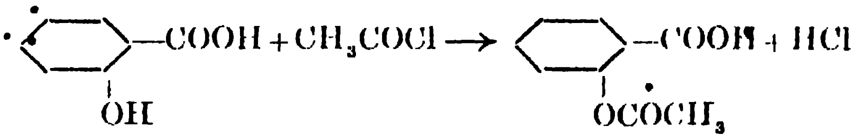
On acidification, salicylic acid precipitates again.

(v) Methyl salicylate, also called **oil of wintergreen,** $C_6H_4(OH)COOCH_3$, is formed by warming salicylic acid and methyl alcohol in presence of strong sulphuric acid.



(vi) Aqueous solution of salicylic acid gives a violet colour with ferric chloride solution.

(vii) Aspirin or acetyl salicylic acid, $C_6H_4(OCOCH_3)COOH$, is made by acetylating salicylic acid with acetyl chloride or acetic anhydride. It melts at 135° and is sparingly soluble in water.



Uses of salicylic acid.—Salicylic acid is a strong antiseptic and is used as a disinfectant. Salicylic acid and sodium salicylate are anti-pyretic (i.e., a drug used to reduce temperature in fever). Salol (phenyl salicylate) is an antiseptic and is used in tooth paste. Methyl salicylate is used in tooth paste and in flavouring confectionary. The use of aspirin for the relief of neuralgic pain and headache is well-known.

Salicylaldehyde, o-$C_6H_4.(OH).CHO$, is ortho-hydroxy benzaldehyde. It occurs in the oils of meadow sweet and other species of Spiraea. It is formed together with its p-isomer, by **Reimer's re-**

action by heating phenol with chloroform and alcoholic potash, and separated by steam distillation—the p-isomer is not readily steam volatile.

$$HO.C_6H_4.H + Cl.CHCl_2 \xrightarrow{KOH} HO.C_6H_4.CHCl_2 \xrightarrow{KOH}$$
$$HO.C_6H_4(OH)_2 \longrightarrow HO.C_6H_4.CHO + H_2O$$

It is a colourless, pleasant-smelling liquid, b.p. 196°, and is moderately soluble in water. It gives a violet colour with ferric chloride and is readily oxidised to salicyclic acid.

XXI

*FOOD AND NUTRITION

Food and diet.—Food is required for the growth and maintenance of human body. Broadly speaking, food is what we eat to live. Its main functions are: (i) to supply heat and energy, (ii) to build and repair the tissues of the body, and (ii) to regulate the internal processes of the body so as to maintain life. For the fulfilment of the above functions food must supply: (a) *fats*, (b) *proteins*, (c) *carbohydrates*, (d) *vitamins* and (e) *mineral salts*. Besides, water and oxygen are essential to all living processes.

The first main function of food is to provide fuel for producing energy in the human body. In this respect the body may be compared to an engine. As an engine cannot move without fuel, so also a human body needs fuel or energy to do work. But our fuel is not coal or petrol but fats and carbohydrates. By slow oxidation inside the body these fuels supply energy which makes both bodily movement and mental work possible.

Fats.—Fats also called *lipids*, can be found in both animal and vegetable foodstuffs. Vegetable fats include cocoanut oil, mustard oil, groundnut oil, and olive oil. Animal fats include butter, ghee, fish oils and mutton fat. Cereals, e g., rice and wheat, contain a small amount of fat. Fat is a more concentrated form of energy than carbohydrates and proteins, and yields more calories, weight for weight. Fats are oxidised to furnish energy and partly *stored* as body fat which acts as a reserve. The reserve is called upon during fast or starvation.

Fats are emulsified in the stomach and split up into fatty acids and glycerine during digestion, largely by the action of the enzyme *lipase* from the pancreas. Oils are more easily digestible than fats.

Carbohydrates.—Carbohydrates are of two kinds: starch and sugars. Starch is obtained mainly from rice and other cereals such as wheat, maize, barley, and millets, and also from sago, tapioca and potatoes, etc. Starch is abundant and is a cheap source of energy. Sugar is obtained from sugar cane, honey and fruits. The carbohydrates enter into the process of nutrition as glucose, formed by their hydrolysis by enzymes. The glucose finds its way into the blood where it is oxidised to CO_2 and water, yielding energy.

The oxidation of glucose is helped by *insulin*, which is secreted by the pancreas into the blood. This secretion is seriously hampered in diabetes, and as such the glucose is not oxidised in diabetes for want of *insulin*. This accounts for the abnormal increase of glucose in the blood and urine of diabetic patients. The digestion of starch begins in the mouth during mastication, where the enzyme *ptyalin* of saliva hydrolyses some of the starch into maltose in slightly alkaline medium, and the process continues in the stomach. Further hydrolysis into glucose is effected by *pancreatic amylase* and other enzymes of the pancreatic juice. Cooked starch is more readily digested, although raw starch can be digested. Glycogen, sometimes called 'animal starch', $(C_6H_{10}O_5)n$, is a reserve food in our liver which is readily converted into glucose when occasion arises.

The carbohydrates serve as fuel, but if the diet is particularly rich in carbohydrate, in excess of the needs of the body, the surplus is *transformed* into fat. Cellulose is not digested in the human body, and hence it has no food value, but it gives bulk to the food residues and thereby assists their passage along the digestive tract.

Proteins. —The second function of food is to supply materials for building up and repair of tissues of the body. The most important building materials are proteins. They are essential constituents of all living cells and *there can be no life without proteins.* Plants synthesise their proteins, but we get our proteins either from plants or animals. It is out of the proteins that flesh, muscle, and various parts of our body, such as brain, liver, kidney and heart, are made.

Foods rich in animal proteins are fish, meat, cheese, egg, and milk. All animal proteins cannot serve in nutrition; egg albumin, for example, is a protein food but gelatin is not. Proteins are found in vegetable products like pulses and nuts and also to a small extent in cereals.

During digestion in the stomach the enzyme *pepsin* of the gastric juice splits up proteins into simpler forms, which are finally degraded into amino acids (p. 55) by the action of enzymes in the intestine. The amino acids pass into the circulating blood. The body synthesises its own tissue proteins out of these aminoacids. Proteins can also serve as fuel. They supply about the same calories as carbohydrates, weight for weight, but the protein is a costlier fuel.

Vitamins. —Our health and growth largely depends upon the presence in foodstuffs of *small* amounts of specific organic substances, called *vitamins*—a name given to them from 'vita' which means life, since they are necessary for life. Vitamins are *accessory food substances* without which in small amounts a body sickens and dies, even if provided with fats, proteins, carbohydrates and mineral salts, since food is not properly absorbed in absence of vitamins. Vitamin deficiency, therefore, causes various disorders and diseases in our system. Vitamins are present in *fresh* foods of various kinds. At least six vitamins are well known, though many more have been reported.

Vitamin A. —It promotes growth. Its deficiency leads to night blindness and an eye disease, called xerophthalmia. Certain fats and oils, such as cod-liver oil, halibut-liver oil and butter, are rich in vitamin A, but it is *not* present in lard, olive oil or margarine.

Vitamin A, as such is not present in vegetable foods. They contain a substance called *carotene* or *provitamin A*. Man produces vitamin A from carotene. Hence foodstuffs which contain carotene are classed as rich in vitamin A.

Green leafy vegetables, carrots and tomatoes are rich in vitamin A. Both land and marine plants contain carotene. The source of vitamin A in milk and milk products is the *green* pastures of the cattle. Fish liver is rich in vitamin A—the source may be traced to the marine plants. Vitamin A is fat soluble and is fairly resistant to heat.

Vitamin B. —It is not a single substance but consists of several B vitamins, e.g., B_1, B_2, B_6, and is commonly known as B-complex. Vitamin B_1, sometimes referred to as vitamin B, regulates the use of carbohydrates in the body. Its deficiency causes *beri-beri*. It is abundent in all *whole cereals* like rice and wheat, in many vegetables and in yeast, but it is absent from *white* flour and *polished* rice and hence the incidence of beri-beri amongst people fed on polished rice. Vitamin A and vitamin B are not easily destroyed by cooking.

Vitamin C. —It is found in fresh fruits, vegetables and sprouted pulses, and especially in lemon, orange, tomato and *amla*. It tends to be destroyed on cooking or storing food. Vitamin C or ascorbic acid is chemically related to the sugars. Its deficiency leads to scurvy. Sailors on long voyages are particularly susceptible to scurvy for want of fresh fruits and vegetables. A liberal supply of lemon juice prevents its occurrence.

Vitamin D.—It promotes growth and works primarily on our bones. Its deficiency causes *rickets* in children and *osteomalacia* (which means 'softening of the bones') in adults, chiefly women. Cod-liver oil and other fish oils are rich sources of vitamin D. Rickets and osteomalacia can be cured by taking cod or shark liver oil. It is also present in milk and milk products and in vegetables. Vitamin D is not easily destroyed by exposure to air or by cooking. Action of ultra violet rays of the sun on our skin produces this vitamin in our system.

Vitamin E. —This vitamin prevents sterilty of man and animals. It is present in leaves of plants, wheat germ oil, and milk. Lettuce and alfaalfa are specially rich in it. It is stable to heat but is readily oxidised.

Vitamin K.- It is present in green plants, specially in alfaalfa. It stops haemorrhage and causes clotting of blood. Animals deficient in this vitamin are in danger of bleeding to death when injured.

Mineral salts.—The mineral salts act partly, along with proteins, as building materials for the formation of bones and teeth, and partly as regulating factors like vitamins—they regulate the functions of body fluids such as blood and digestive juices. About 4 per cent of the human body weight consists of Ca, P, K, Na, S, Mg, Cl, Fe, I, Si and F. Among the 5 metallic elements calcium is the most plentiful (1·5 per cent) in the body—our bones contain calcium phosphate and teeth calcium fluoride. Calcium salts are necessary for the maintenance of heart beats and for coagulation of blood. Milk and green leafy vegetables are the best sources of calcium as well as phosphorus.

Phosphorus is present in bones and muscles, as well as in brain and nerve tissues. Iron is essential for the formation of red haemoglobin of the blood. Shortage of iron causes anaemia. Foods rich in iron are green vegetables, spinach, cabbage, and yolk of egg. Milk, which is otherwise a complete food, is poor in iron. Another important mineral requirement is iodine. Its deficiency causes goitre. The common salt of our food supplies the hydrochloric acid of the gastric juice in our stomach, and also traces of sodium iodide. Sometimes sodium iodide is added in small amounts to the city water supply or to the table salt to avoid the prevalence of goitre.

How much to eat. —The quantity of food that a man takes daily varies with such factors as age, sex, weight, work and climate. A large proportion of the food supplies energy by oxidation in the circulating blood. The energy provided by food is measured in calories. In nutritional science one calorie is the heat required to raise the temperature of 1 kilogram of water by one degree centigrade. Different foodstuffs have different values in terms of calories. The fuel values of protein and carbohydrate are approximately 4 calories per gram, while that of fat is 9 calories per gram. The energy requirement of an average man weighing about 150 lbs. and doing moderate muscular work is about 3520 calories a day. At a rough estimate a man in India requires on an average 2500 to 3500 calories a day, while an Indian woman needs 2100 to 2800 calories a day, varying with the nature and amount of work.

Heavy manual workers obviously need more: stone mason 4400 calories, wood cutter 5000 calories. A brain worker is amply supplied by a diet of 2200 to 2600 calories. Nursing mothers need more calories than that quoted for average woman. Growing children require as much food as an adult manual worker.

The weights of different foodstuffs necessary to supply the required calories is then calculated from their energy or fuel values. A satisfactory division of the elements of food in the daily diet giving 3000 calories is: 100 gm. protein, 100 gm. fat and 400 gm. carbohydrate, and a certain quantity of minerals and vitamins. A typical diet contains about one-sixth of fat, one-sixth of protein and two-thirds of carbohydrates.

A balanced diet.—The different kinds of food taken together constitute a diet, and a satisfactory diet should: (i) contain necessary amounts of each of the essential elements of food, namely, fat, protein, carbohydrate, mineral salts, and vitamins, (ii) supply adequate calories. A diet which is so distributed is known as a *balanced diet*. The diet must also conform to dietetic habits of the people concerned. Typical balanced diet suitable for India is as follows:

Food materials	*Vegetarian*	*Non-vegetarian*
Cereals (including wheat)	20 oz.	20 oz.
Vegetables	12 ,,	8 ,,
Pulses	3 ,,	3 ,,
Fruits	2 ,,	2 ,,
Milk	8 ,,	8 ,,
Fats and oils	2 ,,	1 ,,
Sugar	2 ,,	2 ,,
Meat, fish & eggs	...	4 ,,
	49 ,,	48 ,,
Less 5 per-cent. for wastage	2.5 ,,	2.5 ,,
Net	46.5 oz.	45.5 oz.

But the present Indian diet amounts only to between 20 and 30 oz. in the day, and that also revolves practically round cereals (about 16 oz.), e.g., rice, wheat and millets. The cereals are all rich in carbohydrates and hence their energy value is high. But they also contain a little fat, protein and mineral salts. Cereals are not very rich in iron and calcium but fairly rich in phosphorus. Rice is 75-80% starch and is a poor source of vitamins and calcium. Proteins, vitamins, and minerals are lost in milled and polished rice, but they are retained in *parboiled* rice. Wheat (65-70% starch) has the largest protein content (about 14) of all cereals, while rice has the lowest. Wheat also contains a little more calcium and is richer in B vitamins than rice, and hence a better food. Pulses are richer in proteins than cereals, and hence it is called 'poor man's meat'. Sprouted pulse contains vitamin C. Fruits supply vitamins and mineral salts. Citrus fruits (lemons and oranges) are particularly rich in vitamin C. The nearest approach to a complete food is milk. It contains fat, carbohydrate, high quality protein, mineral salts like calcium and phosphorus, and A, B, C and D vitamins. Fish is an important food; it is a good store of proteins, vitamins A and D, and phosphorus. Mutton and other forms of meat are rich in proteins. Next to milk, eggs are all-round food. Eggs contain more of vitamin A and iron than milk. So, we know what there is to eat.

XXII

ORGANIC MANIPULATION

Purification of organic compounds. —The first step in the investigation of an organic substance is to obtain it in a pure state. Whether the organic compound is isolated from a natural source or prepared in the laboratory, the initial product is seldom pure and is usually a mixture and hence its purification involves its separation from other substances. Common methods of purification are: (i) *crystallisation*, (ii) *sublimation*, (iii) *distillation*, and (iv) *extraction with a solvent*.

Crystallisation from a suitable solvent is very effective for the purification of organic solids. A suitable solvent (or a mixture of solvents) is chosen, and the crude substance is then dissolved in the *minimum* quantity of the *hot* solvent—heating being done on water bath, in case of inflammable solvents, and using a reflux condenser (p. 52). When the hot solution is clear and contains no insoluble impurities, it is taken in a basin and allowed to cool in cold water or ice, when crystals separate. But if the hot solution contains insoluble impurities, it is filtered before cooling—the filtration is done through a hot water or steam-jacketed funnel (p. 42, part I) in order to prevent crystallisation in the funnel. *A fluted* filter paper and a funnel with its steam cut off are also used for the filtration of a hot solution. The filtrate is left for crystallisation in a porcelain basin. After the

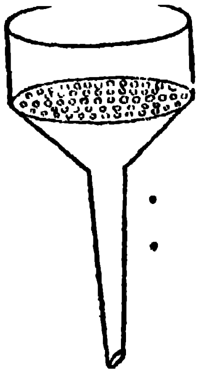


Fig. 8

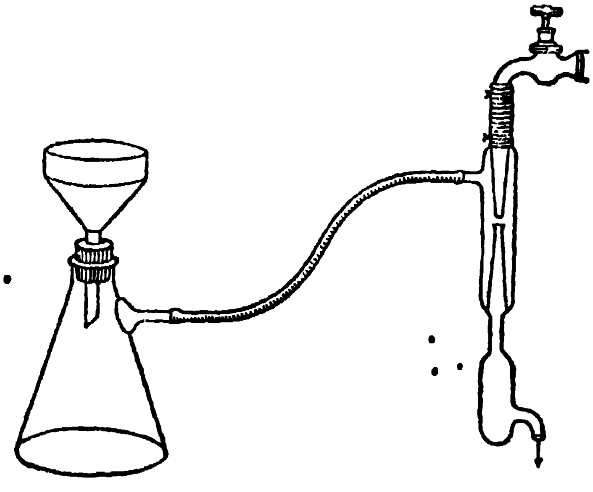


Fig. 9.

crystallisation is complete, the crystals are filtered with the aid of a suction filter (fig. 13, part I and fig. 9).

A Buchner funnel (fig. 8) of correct size to contain the crystals is tightly fitted into the neck of a *Buchner filtering flask* (fig. 9) through a rubber cork, and a filter paper of right size (just to cover the holes of the perforated plate of the funnel) is placed in position. The side arm of the flask is connected to a water pump by a length of pressure rubber tubing. To start filtration, the filter paper is moistened with the solvent, suction is applied, and the crystals are quickly transferred into the funnel—any residual crystals in the basin are washed into the funnel by means of a little fresh solvent. After most of the mother liquor is drained off, the crystals are washed once or twice with minimum amount of *cold* solvent under gentle suction in order to remove the adhering mother liquor. The crystals are then pressed with a spatula or glass stopper. When no more liquid filters, the pump is disconnected, and the crystals are taken in a sheet of filter paper or a watch glass.

To filter small quantities of solids, a small funnel *with a loose perforated porcelain disc* is preferred—a piece of filter paper is cut to size and placed in the disc so as to lap up the sides a short distance. The funnel is tightly fitted through a rubber cork to a stout and wide test tube having a side arm (fig. 10) which is connected to the water pump.

If the substance under investigation is a mixture of solids and if they all dissolve in the hot solvent—the least soluble of the solids would first deposit as crystals on cooling, and the mother liquor will give a second crop of crystals containing a larger proportion of the more soluble constituent. By repetition of this process of *fractional crystallisation*, the constituents of the mixture may be separated more or less in a pure form.

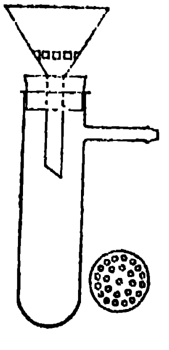


Fig. 10.

Treatment with animal charcoal is a common method to purify and decolorise organic substances which are contaminated with coloured or resinous impurities. Crude acetanilide, for example, is purified by boiling its aqueous solution for some time with animal charcoal (about 5% of the weight of the substance), and then filtering hot—the filtrate deposits colourless crystals of acetanilide on cooling.

The drying of the crystals is the final step in the process. The crystals are often dried by placing them in folds of filter paper, and then by standing in air. Drying may also be done by placing the crystals on a watch glass in a desiccator (or better a vacuum desiccator) (fig. 30, part I) containing substances like granular calcium chloride or concentrated H_2SO_4 which would absorb the vapours of the solvent used for crystallisation or washing. The crystals of relatively high melting point may be dried in a steam oven. Hygroscopic solids must be dried in a desiccator.

A small sample of the crystals may be dried by pressing with a spatula on to a porous plate, and its purity ascertained by determining the melting point.

Choice of a suitable solvent is a matter of utmost importance in crystallisation. A suitable solvent dissolves much more of the solid *when hot than when cold*, so that the hot saturated solution deposits a portion of the solid as crystals on cooling. The right solvent is found out by trial. A little of the crude solid (0·05—0·1 gm) is treated with 0·5—1 c.c. of some solvent ; if the solid dissolves in the *cold* or remains insoluble even on heating, the particular solvent is regarded as unsuitable. If, however, the solid dissolves in a maximum of 3—4 c.c. of the boiling solvent, but crystallises out readily on cooling, the solvent under trial is chosen, and if not, another is tried.

Water is a very common solvent. Other solvents usually employed are : (i) *ethyl alcohol*, *b.p.* 78°C, (ii) *ether*, *b.p.* 35°C, (iii) *acetone*, *b.p.* 56°, (iv) *benzene*, *b.p.* 80°C, (v) *glacial acetic acid*, *b.p.* 119°C, (vi) *chloroform*, *b.p.* 61°C, (vii) *carbon tetrachloride*, *b.p.* 78°, (viii) *ethyl acetate*, *b.p.* 77°C, and (ix) *petroleum ether*, available in different fractions having boiling points ranging from 40° to 120°C.

If a solid happens to be almost insoluble in one solvent, but too much soluble in another, then a mixture of two such solvents, called **mixed solvents,** e.g., (i) *benzene and chloroform*, (ii) *benzene and petroleum ether*, etc., may often prove useful as a solvent.

Sublimation.—Occasionally an organic solid is purified by sublimation—volatile solids, e.g., camphor, naphthalene, benzoic acid, sublime, while the non-volatile impurities are left behind. There are various ways of carrying out sublimation. In one method the crude solid, e.g., camphor, is taken in a porcelain basin and covered with a sheet of filter paper having some perforations on it—the filter paper is held in position by a funnel. The basin is heated on a sand-tray by a small flame, when the camphor subilmes and deposits as colourless crystals on the filter paper and any non-volatile impurity remains in the basin.

Distillation. —Distillation is a common method of purification of organic liquids which boil without decomposition. Volatile liquids can be separated from non-volatile impurities by distillation.

The liquid is placed in a distilling flask fitted with a condenser and receiver (fig. 19, part I)—the neck of the flask is closed with a cork through which a thermometer passes in such a way that its bulb is *just below* the opening of the side-tube. A few pieces of porous tile are placed in the liquid to prevent bumping. The flask is then carefully heated on a wire guaze, water bath, sand bath or metal bath (depending on the liquid to be distilled).

In case of high boiling liquids or when a small amount of a liquid is to be distilled, the flask may be directly heated with a free flame (using, however, a rotary motion of the flame).

The mercury column in the thermometer rises quickly as soon as the liquid begins to boil and then remains practically stationary until almost the entire liquid is distilled. Towards the end of distillation, the temperature may show a rise due to supper-heating, when the distillation is stopped. When a single liquid (which may contain non-volatile impurities) is treated, the temperature does not fluctuate during distillation.

In case of liquids which boil above 130°C or so, the condenser is omitted and a long glass tube is used as an air condenser.

Fractional distillation. —When no constant boiling point is observed during distillation, it is an indication that the liquid is not a single substance but a mixture.

It is often possible to separate two liquids by a single distillation, provided that their boiling points are wide apart and differ by 40°C or more, e.g., benzene, b.p. 80°, and nitrobenzene, b.p. 209°. When distilled the more volatile liquid first passes over, the temperature then quickly rises and the higher boiling liquid distils—the distillates are collected in separate fractions. A second distillation is often necessary to obtain the liquids in a pure state.

When, however, the boiling points of the liquids lie close together, a single distillation causes a very incomplete separation. In such cases the liquids are separated by *fractional distillation using a fractionating column* (fig. 21, part I).

The liquid mixture benzene (b.p. 80°) and toluene (b.p. 110°), for example, is distilled in a round flask fitted with a fractioning column (which is inserted between the flask and the condenser) (fig. 11).

The vapour from the boiling liquids is richer in the more volatile component. As the current of vapour passes up the column, the vapour of the higher boiling liquid is more readily condensed, so that the vapour above the condensed liquid becomes still richer in the more volatile component. The condensed liquid runs down the column and in its return flow washes the rising current of vapour. The vapour leaving the column at the top is richer in the more volatile component—it passes off by the condenser and is collected as a distillate in the receiver. The distillate is richer in the more volatile benzene than the original liquid. The liquid remaining in the flask is richer in the less volatile component toluene. Only partial separation is effected by this means. The fractions are re-distilled, when the distillate become still richer in benzene, and the residual liquid in the flask in toluene. Fractionation is repeated until fractions of constant boiling points are obtained. These fractions are taken as pure liquids.

Sometimes complete separation is not possible, as many liquids form *constant boiling mixture*, e.g., alcohol and water (p. 27).

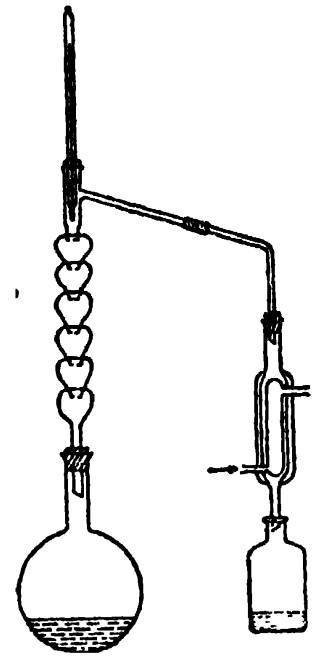


Fig. 11

Distillation under reduced pressure.—If a liquid, e.g., glycerine, decomposes near its boiling point when distilled at atmospheric pressure, it may be distilled under reduced pressure which naturally lowers the boiling point, (p. 50, part I)—the lowering depends upon the extent of vacuum created inside the distilling flask. Distillation and fractional distillation are, therefore, carried out under reduced pressure in the case of liquids which are likely to decompose near their boiling points at atmospheric pressure. Distillation under reduced pressure is also called **vacuum distillation** or **distillation in vacuo.**

The distillation is usually carried out in a two necked *Claisen flask* (fig. 22, part I) whose side-tube is connected, via a condenser, with a pump and pressure gauze. The thermometer is inserted into one neck of the flask and through the other passes a tube drawn out to a fine capillary, reaching nearly to the bottom of the flask. When the pump is started, air bubbles are drawn thorugh the liquid, which prevents bumping and helps regular boiling. The condenser is attached to 2 (or more) receivers (to collect different fractions) through an adapter.

The liquid to be distilled is placed in the flask and the pump is started—air bubbles are drawn through the capillary. As soon as the pressure becomes sufficiently low (as the pressure gauze indicates), the distillation is started by cautiously heating the flask with a constantly moving, almost luminous flame. By rotating the adapter the different fractions are made to fall in one or the other receiver without breaking the vacuum during distillation.

The distillation unit may be attached to a water pump, when high vacuum is not required. Vacuum distillation can also be carried out in ordinary distilling flask (fig. 216).

Organic liquids must be carefully dried before distillation.—This is generally done by adding solid dehydrating agents, e.g., the anhydrous salts like $CaCl_2$, K_2CO_3, $MgSO_4$, and Na_2SO_4, or solid caustic potash, in the liquid and corking the container, and then allowing the liquid to stand several hours in contact with the drying agent until the liquid is clear. The liquid is then filtered and the filtrate ready for distillation.

Steam distillation.—The method of steam distillation is often used in the isolation and purification of organic compounds—both solid and liquid. The method has been discussed with reference to the distillation of aniline (p. 89) in a current of steam.

Extraction with solvents.—Many organic compounds can be isolated from their aqueous solutions (or suspensions) by extraction with an organic solvent in which they are much more soluble than in water. Ether, benzene, petrol and chloroform, etc., are often used for extractions, as their solubility in water is very low and therefore form separate layers. Ether is a common solvent as it is inert and can be readily removed at relatively low temperature, b.p. of ether being only 35°C.

The aqueous mixture, e.g., phenol in water, is taken in a separating funnel and a small quantity of ether added—the funnel is then gently shaken, and then allowed to rest. Ether and water separate in two layers—the phenol dissolves in ether which floats on the top of the aqueous layer. The aqueous layer is first run off and then the ether extract. Successive extractions are made with the solvent. The extracts are wet. The combined extracts are dried with anhydrous $CaCl_2$ until clear, and then filtered. The solvent is carefully distilled off on a water bath—the phenol remains as a liquid residue.

In extraction with ether or benzene, the organic solvent, being lighter than water, floats on the aqueous layer, but chloroform, being heavier than water, sinks below the aqueous layer. Caffeine may be extracted with chloroform from aqueous tea liquor.

Successive extractions with small amount of a solvent are more effective than a single extraction with the same total amount of the solvent. If in a mixture of two liquids, e.g., alcohol and benzene, one is soluble in water and the other is not, it is possible to separate the insoluble liquid. The liquid pair, e.g., alcohol and benzene, is shaken with water in a separating funnel and allowed to rest—benzene, being insoluble and lighter than water, separates and floats on the aqueous layer of alcohol. The aqueous layer is run off and separated from benzene.

Tests of purity.—A pure solid generally looks homogeneous when examined under a microscope, and if crystalline, the crystals all appear alike. But the best test for the purity of an organic solid is its *sharp melting point.* A pure solid melts sharply at a correct temperature within a range of about 1°. Melting point, therefore, is an index of the *purity* of a solid and is used for *identification* of unknown solids.

Most organic solids melt below 300° and at a definite temperature, but there are some which melt with decomposition. Impurities nearly always lower the m.p. of a solid, and also makes it indefinite. It is also essential that the solid must be *dry*, as a trace of moisture may greatly lower the melting point.

Determination of melting point.—A clean and dry soft glass test tube is heated in a Bunsen flame until it is soft, when it is drawn into a thin-walled capillary tube. The capillary is cut into a short length (6—8 cm.) and sealed at one end by holding over a flame.

A little of a carefully dried solid is placed on a clean porous plate and finely powdered by pressing and rubbing with the end of a spatula. The open end of the capillary is then gently stabbed several times on to the powdery solid, and each time the closed end of the capillary is tapped on the plate until a tightly packed layer of the solid (2—3 mm.) is formed at the bottom.

The melting point bath (fig. 12) is generally a boiling tube or a small beaker (50 c.c. capacity) containing concentrated sulphuric acid—

a crystal of nitre is added to oxidise any charred matter and also to prevent the liquid from being discoloured. The sulphuric acid bath may be used up to about 260°C, but there is a risk of serious injury if the bath breaks. For temperatures up to 210°C liquid paraffin or glycerol is a suitable and safe liquid to use.

The thermometer (reading up to 360°C) is removed from the melting point bath and the capillary (with the packed solid in it) is lightly pressed against the moistened (with the liquid of the bath) end of the thermometer so that the enclosed solid is opposite the middle of the bulb —the tube adheres to the bulb by capillary action. The thermometer (with the capillary) is then suspended in the melting point bath with its bulb a few mm. below the surface of the liquid. The bath is heated gently and steadily with a small flame, and the temperature at which the solid melts, i.e., becomes a transparent liquid, is noted.

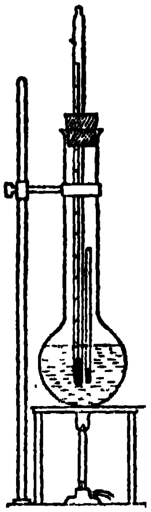


Fig. 12

Exercise.—Find the melting point of naphthalene (m.p. 80°C) and benzoic acid (m. p. 121°C).

Identification by mixed melting point.—If an unknown solid X, by reason of its m.p., is suspected to be a particular substance A, then about equal amounts of X and A are intimately mixed together, and the m.p. of the mixture is determined.

If X and A are identical, the mixture would have the same m.p. as A. But if X and A are not the same, the m.p. of the mixture would be less than that of either and also indefinite. The method of mixed melting point is helpful in identifying unknown solids.

Determination of boiling point.—A pure liquid, which boils without decomposition, has a *constant* and *definite* boiling point at a given pressure. The b.p. affords a valuable means of identifying an organic liquid.

A constant boiling point is not necessarily a test of the purity of a liquid, as it may be due to a constant boiling mixture (p. 27, part I.).

A boiling tube (or a small distilling flask) is fitted for distillation (fig. 13), and a few c.c. of the liquid is placed in it. Two or three pieces of porous title are added to the liquid in order avoid bumping. A thermometer is then inserted so that the bulb is well above the liquid and *does not dip in it*. The liquid is gently heated by means of a small flame until it boils and distils at the rate of 1—2 drops a second. The stem of the thermometer is completely immersed in the vapour during distillation.

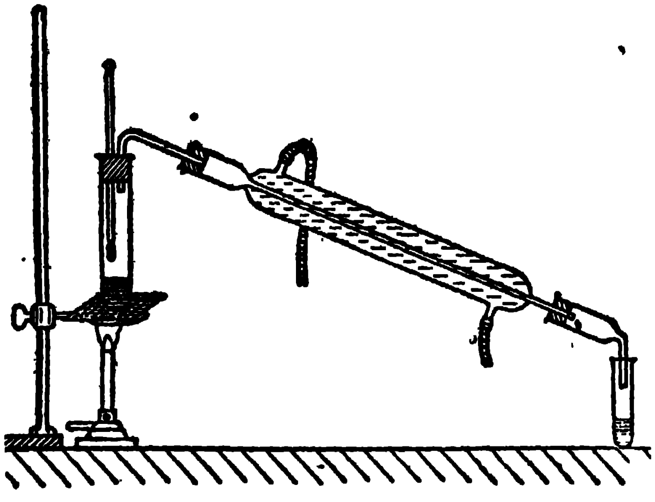


Fig. 13

The mercury column rises rapidily in the thermometer as soon as the liquid boils and then remains practically *stationary* until nearly the entire liquid is distilled. The constant temperature is noted and is the boiling point.

XXIII

ANALYSIS OF ORGANIC COMPOUNDS

Qualitative analysis.—After an organic compound has been prepared in a *pure* state, the next step is to detect its constituent elements.

Detection of carbon and hydrogen.—Carbon and hydrogen are detected by oxidising an organic substance with copper oxide, when carbon dioxide and water are formed.

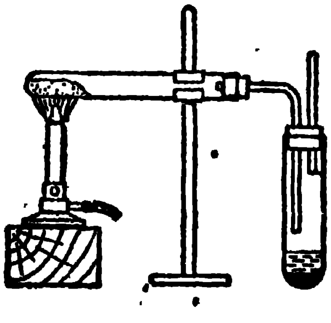


Fig. 14

The *dry* substance (0·5 gm.), e.g., cane sugar, is mixed with 20—25 times its weight of *dry* and fine copper oxide in a mortar, and the mixture is then placed in a hard glass test tube. The tube is fitted with a cork and a delivery tube which dips into lime water (fig. 14). On strongly heating the mixture, any carbon present is oxidised to CO_2 which bubbles into lime water and turns it milky, and any hydrogen present is oxidised to H_2O which deposits in drops on the cooler part of the test tube—the liquid drops turn anhydrous copper sulphate blue and are confirmed as water. The formation of water indicates the presence of hydrogen, provided the substance and copper oxide are thoroughly *dried* before the experiment.

Copper oxide is hygroscopic, and hence it is strongly heated and then cooled in a desicator before use in organic analysis.

When the organic compound is a gas or a volatile liquid like ether and alcohol, the gas or the vapour of the liquid is passed over red-hot CuO, and then through lime water.

Organic substances are frequently inflammable, and readily catch fire or char and swell up into a black mass on heating in a crucible lid.

Detection of nitrogen.—Many organic nitrogen compounds evolve ammonia when strongly heated with sodalime. Evolution of ammonia proves the presence of nitrogen, but a negative result does not show absence of nitrogen, since there are some organic compounds containing nitrogen, e.g., nitro and azo compounds, which do not evolve ammonia on heating with soda lime.

But *Lassaigne's test* for nitrogen is applicable to every type of organic nitrogen compound.

Lassaigne's test for nitrogen, sulphur, and chlorine, bromine, and iodine.—The method depends on the fact that when an organic compound is strongly heated with *metallic sodium*, any nitrogen present is converted into sodium cyanide, sulphur into sodium sulphide, and the halogens into sodium halides, which are then tested.

A piece of metallic sodium, about the size of a pea, is melted in a short test tube by heating over a small flame, and a little of the organic compound (0·02—0·05 gm.) is dropped directly over the molten metal. A vigorous reaction sets in and care is necessary.

The mixture is strongly heated for 2—3 minutes until the glass is red-hot. The red-hot tube is then plunged in distilled water (about 5 c.c.) in a mortar, whereby the hot end of the tube crumbles—the plunging should be done in such a way that the eye is not endangered, as any unused sodium would react with water with a flash and may cause explosion.

The contents of the mortar are then ground with a pestle, and filtered from powdered glass and carbonaceous matter. The filltrate is *alkaline*, because any unused sodium reacts with water, producing caustic soda. The filtrate contains sodium cyanide, sodium sulphide and sodium halides, if nitrogen, sulphur and halogens are present in the original substance. The filtrate is tested for as follows:

(a) **Nitrogen.**—To a portion of the alkaline filtrate about 1 c.c. of ferrous sulphate solution is added, and the mixture boiled for a minute or so. The solution is cooled and a drop of ferric chloride solution is added, and then acidified with dilute hydrochloric acid, when the formation of a blue colour or precipitate detects the presence of nitrogen.

During fusion the nitrogen and carbon in the substance combines with metallic sodium, giving sodium cyanide. When the alkaline filtrate is treated with ferrous sulphate, ferrous hydroxide is precipitated and then sodium ferrocyanide, $Na_4[Fe(CN)_6]$, is formed in the solution. On the addition of ferric chloride and acidification deep blue ferric ferrocyanide (Prussian blue) $Fe_4[Fe(CN_6]_3$, is formed.

$$\begin{aligned}
Na + C + [N] &= NaCN \text{ (sodium cyanide).}\\
FeSO_4 + 2NaOH &= Fe(OH)_2 + Na_2SO_4\\
Fe(OH)_2 + 6NaCN &= Na_4Fe(CN)_6 + 2NaOH\\
FeSO_4 + 6NaCN &= Na_4Fe(CN)_6 + Na_2SO_4\\
3Na_4Fe(CN)_6 + 4FeCl_3 &= Fe_4[Fe(CN)_6]_3 + 12NaCl
\end{aligned}$$

(b) **Sulphur.**—To a portion of the alkaline filtrate few drops of sodium nitroprusside solution are added, when a violent colour develops due to the presence of sulphide.

During sodium fusion any sulphur prseent in the substance is converted into sodium sulphide, and hence the detection of sulphide indicates the presence of sulphur.

(c) **Chlorine, bromine and iodine.**—*In absence of nitrogen and sulphur* (as indicated by the tests above) a portion of the alkaline filtrate is acidified with dilute nitric acid and a solution of silver nitrate added—a curdy white or yellow precipitate indicates a halogen. since during fusion with metallic sodium any Cl, Br or I present in the substance are converted into sodium chloride, bromide, or iodide. The precipitate is distinguished as follows:

Procipitate	Solubility in ammonia	Indicates presence of :
Curdy white AgCl	Readily soluble	Chlorine
Pale yellow AgBr	Difficultly soluble	Bromine
Yellow AgI	Insoluble	Iodine

For further tests a portion of the filtrate is acidified with hydrochloric and then treated with chlorine water and shaken with carbon disulphide : (i) a reddish-brown CS_2-layer indicates bromine, and (ii) a violet layer iodine.

In presence of nitrogen and/or sulphur the filtrate is acidified with dilute HNO_3 and then boiled for some minutes to decompose any NaCN and Na_2S present and to expel the liberated HCN and H_2S. The solution is then cooled and tested with silver nitrate. A curdy white or yellow precipitate indicates halogen.

Beilstein's test for halogens.—An inflammable organic halogen compound often gives a green-edged flame. But a more delicate test, due to Beilstein, is to heat the substance with copper oxide when a bright green flame is produced.

One end of a thick copper wire (4 inches) is inserted into a cork, and about ½ in. of the other end is bent over so that it lies parallel to the longer length of the wire. The bent end of the wire is heated in a Bunsen flame until it ceases to colour the flame green—the end is now coated with copper oxide. It is cooled and dipped into the substance and again heated, when the flame is tinged with green. The test depends on the formation of volatile copper halide. The test may sometimes fail, and also occasionally given by compounds free from halogens. Thus many organic nitrogen compounds give this test due to the formation of cuprous cyanide.

Detection of phosphorus.—When an organic phosphorus compound is fused with an oxidising mixture of sodium carbonate and nitre, the phosphorus is converted into alkali phosphate. The fused mass is extracted with hot water—the filtrate is acidified with nitric acid and then warmed with ammonium molybdate solution, when the formation of a yellow precipitate detects phosphorus.

Detection of oxygen.—There is no satisfactory general test for detection of oxygen in organic compounds. Its presence is deduced from the results of quantitative analysis.

Middleton's alkali-sugar test for sulphur and halogen and nitrogen (in a limited number of cases).—A small sample of the substance is mixed with 5 times its weight of alkali-sugar mixture (a mixture of 9 parts of pure anhydrous Na_2CO_3 and 1 part of pure cane sugar) and then heated and proceeded for detection of S, halogens and N, as in Lassaigne's test, except that 2—3 drops of aqueous NaOH are to be added to the filtrate before testing for nitrogen.

Middleton's alkali-zinc test for nitrogen.—A small amount of the substance is mixed with 5 parts of its weight of alkali-zinc mixture (a mixture of 1 part of anhydrous Na_2CO_3 with 2 parts of zinc dust) and then heated and treated as in Lassaigne's test.

***Quantitative analysis.**—The qualitative analysis of organic compounds is followed by their quantitative analysis (also called *ultimate analysis*) by which the actual amounts of the elements present in a compound are determined.

Estimation of carbon and hydrogen.—The quantitative estimation of carbon and hydrogen in an organic compound is carried out by oxidising the substance in a current of oxygen, and collecting and weighing the carbon dioxide and water formed. This method of analysis was mainly due to Liebig (1831).

The combustion is carried out in a hard glass tube (fig. 15) which contains (i) a spiral of oxidised copper gauze (B), then (ii) a small

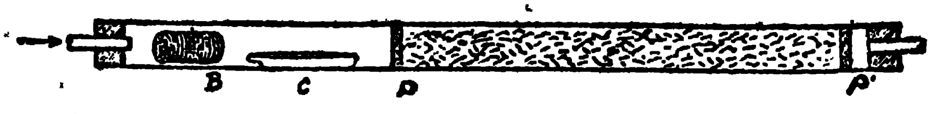


Fig. 15

porcelain boat (C) containing a weighed quantity of the substance (0·1—0·2 gm.) and (iii) finally a layer of *dry* wire-form copper oxide (P to P′) filling nearly two-thirds of the tube, kept in position by loose asbestos plugs.

The tube (d) is placed in a combustion furnace (fig. 16), and the end nearest to the boat is attached to a gas holder (b) containing air and a cylinder of compressed oxygen (a) *via* two wash bottles (c) containing concentrated caustic alkali and sulphuric acid respectively to purify the air and oxygen from carbon dioxide and moisture. The other end of the tube is connected to a weighed U-tube (e) containing granular calcium chloride and a potash bulb (containing strong caustic potash solution) with an attached calcium chloride tube (f) to prevent the loss of moisture from the bulb. The potash bulb with the $CaCl_2$-tube is also previously weighed. Then follows a $CaCl_2$-tube (g) to prevent diffusion of atmospheric moisture inside the apparatus. All corks and rubber connections must be gas-tight..

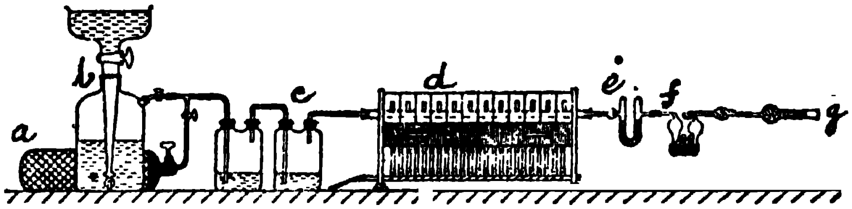


Fig. 16

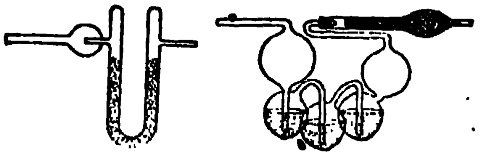


Fig. 17

The operation of combustion is carried out as follows A slow stream of oxygen is first passed through the tube by turning on the oxygen supply, then the layer of copper oxide and next the roll of oxidised copper gauze are made red-hot by lighting the burners under them. The substance is then gradually heated by lighting the burners under the boat itself, and burnt. The oxidised Cu-gauze (B) prevents backward diffusion of the products of combustion. The copper oxide layer (pp′) oxidises any of the substance which may vaporise unchanged, and also converts any CO (formed due to incomplete combustion) into CO_2.

The water that is formed is absorbed in the $CaCl_2$-tube, and the CO_2 in the potash bulb. When the substance is completely burnt, the oxygen supply is cut off, and the apparatus is allowed to cool down in a slow current of dry air. The entire operation of combustion takes 2—3 hours.

The $CaCl_2$-tube and the potash bulb are disconnected, and their ends closed with rubber caps, and finally weighed. The increase in weights of the $CaCl_2$-tube and the potash bulb gives the weights of water and CO_2 formed respectively.

Calculation.—Let the weight of substance taken = *w* gm.

The increase in weight of potash bulb = a gm.

The increase in weight of $CaCl_2$--tube = b gm.

weight of CO_2 formed = a gm.; weight of water formed = b gm.

$$\text{percentage of carbon} = \frac{12}{44}\times\frac{a}{w}\times100 = \frac{300\times a}{11\times w}$$

$$\text{Percentage of hydrogen} = \frac{2}{18}\times\frac{b}{w}\times100 = \frac{100\times b}{9\times w}$$

If the organic substance *contains nitrogen*, a roll of (unoxidised) copper gauze is placed in the combustion tube beyond the copper oxide layer, and kept red-hot during combustion, this will reduce any oxides of nitrogen which would otherwise be absorbed in the potash bulb.

In case it contains *halogens* or *sulphur*, the copper oxide is replaced by fused granulated lead chromate, which retains the halogens as lead halide and the sulphur as lead sulphate, as otherwise the free halogens and SO_2 are liable to be absorbed in the potash bulb and vitiate the result.

Example.—0·1793 gm. of acetone containing carbon, hydrogen, and oxygen only, gave on combustion 0·4082 gm. carbon dioxide and 0·1670 gm. of water. Find its percentage composition.

Weight of the substance burnt = 0·1793 gm. Wt. of CO_2 = 0·4082 gm.; wt. of H_2O = 0·1670 gm.

$$\therefore\ \%\text{ of C} = \frac{300\times0{\cdot}4082}{11\times0{\cdot}1793} = 62{\cdot}07;\ \%\text{ of H} = \frac{100\times0{\cdot}1670}{9\times0{\cdot}1793} = 10{\cdot}35$$

$\therefore$ percentage of oxygen = 100 − (62·07 + 10·35) = 27·58.

Estimation of nitrogen.—Nitrogen in an organic compound is usually estimated by: (i) *Dumas' method* in which all the nitrogen contained in the organic substance is liberated as free nitrogen gas, and (ii) *Kjeldahl's method* in which the nitrogen is liberated as ammonia.

Dumas' method.—The method is based on the fact that when an organic compound containing nitrogen is strongly heated with copper oxide, it is entirely decomposed into carbon dioxide, water and nitrogen (and its oxides)—the products of combustion are then passed over heated copper gauze to reduce the oxides of nitrogen, and finally the nitrogen is collected in a graduated tube over caustic potash solution which absorbs the carbon dioxide. The percentage of nitrogen is calculated from the volume of nitrogen obtained from a given weight of the substance. The analysis is carried out in a combustion tube (fig. 18) which contains: first a spiral of oxidised copper gauze, b, then an intimate mixture of the organic compound (0·15—0·5 gm.) and 10—20 gm. of fine copper oxide, and next a layer of wire-form copper oxide, c, and finally a spiral of bright (unoxidised) copper gauze, d. A hard glass test tube, a, containing magnesite (magnesium carbonate) or sodium bicarbonate, is attached to one end of the combus-

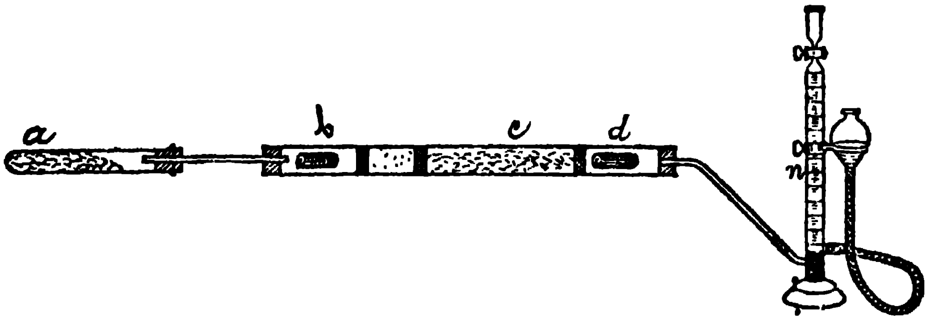


Fig. 18

tion tube, and a Schiff's nitrometer, n, containing 40 per cent caustic potash solution is connected to the other end. The nitrometer consists of a graduated tube fitted with a stop-cock at the top, and having two side tubes, one being attached to the combustion tube, and the other to a reservoir of caustic potash solution. Before the substance is heated, all the air from the apparatus is displaced by a slow current of carbon dioxide—all the while the stop-cock of the nitrometer is kept open and the reservoir is lowered so that the potash solution is run out of the nitrometer tube. When all the air is driven out, the nitrometer is completely filled with the potash solution by raising the reservoir, and the stop-cock is then closed.

The combustion is then started: first the wire-form copper oxide, and then the two copper gauze spirals are heated to bright redness by lighting the burners of the furnace, and finally the mixture of the substance and copper oxide is carefully heated until gases cease to be evolved—the current of carbon dioxide is slackened but not stopped during combustion. When the evolution of nitrogen has ceased, the flow of CO_2 is increased to drive out the last trace of nitrogen into the nitrometer. The apparatus is then allowed to cool. The reservoir is then raised until the potash is at the same level in it and in the nitrometer tube—the volume of nitrogen is then read, and the temperature and barometric pressure are also noted.

Calculation.—Let weight of the substance taken = w gm. Volume of N_2 collected = v c.c. Temperature = t°C. Aqueous tension at t°c = f mm. Barometric pressure = P mm.

Let the volume of the N_2 gas at N.T.P. = v′ c.c.

$$\therefore \quad v' = \frac{v \times (P - f) \times 273}{(273 + t) \times 760} \text{ c.c. at N.T.P}$$

22400 c.c. N_2 at N.T.P. weigh 28 gm. (gram molecular weight of N

$\therefore$ v′ c.c. of N_2 at N.T.P. weigh 28v′/22400 gm

$$\text{percentage of } N_2 = \frac{28v' \times 100}{22400 \times w} = \frac{v'}{8w}$$

Example.—0·1616 gm. of an organic compound containing nitrogen gave 25 c.c. of nitrogen measured at 17°C and 754 mm. pressure. Aqueous tension at 17°C is 14·5 mm. Calculate the percentage of nitrogen in the substance.

$$\text{Volume of } N_2 \text{ at N.T.P.} = \frac{25 \cdot (754 - 14 \cdot 5) \cdot 273}{(273 + 17) \cdot 760} = 22 \cdot 92 \text{ c.c.}$$

$$\text{percentage of } N_2 = \frac{22 \cdot 92}{8 \times 0 \cdot 1616} = 17 \cdot 73.$$

(ii) **Kjeldahl's method.**—The method is based on the fact that when many nitrogenous organic compounds are completely decomposed with hot concentrated sulphuric acid, their nitrogen is converted into ammonium sulphate.

A weighed quantity (0·5—5 gm.) of the substance is taken in a Kjeldahl flask (fig. 19) and covered with about 20 c.c. of concentrated sulphuric acid to which some 10 gms. of potassium sulphate are added. The potassium sulphate raises the boiling point of the acid and promotes oxidation. A small

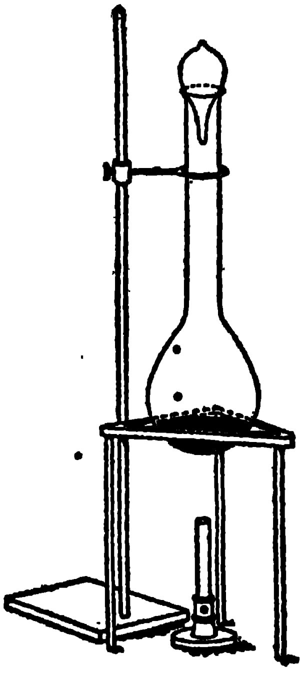


Fig. 19

crystal of copper sulphate which acts as a catalyst is also sometimes added. The flask is then heated for nearly an hour, at first slowly and then sufficiently to boil the acid. The acid first darkens in colour and then becomes colourless. The nitrogen contained in the substance has been converted into ammonium sulphate by this time.

The flask is then cooled and its contents are transferred into a round-bottom-flask (fig. 20) by carefully washing with water. This flask is connected through a trap (a device to prevent carry-over of the liquid from the flask into the condenser) to a condenser which just dips into *a measured volume of standard acid* (N/10 HCl or H_2SO_4) in a conical flask (fig. 20).

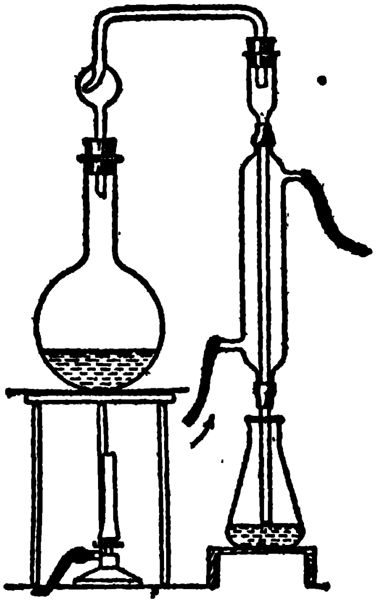


Fig. 20

The liquid in the flask is made strongly alkaline with caustic soda solution to liberate ammonia from the ammonium sulphate, and then boiled to drive off the liberated ammonia which is absorbed in the standard acid. When no more ammonia comes over, the excess acid in the conical flask is back titrated with standard caustic soda solution so as to find the acid neutralised by the ammonia. Hence we can find out the amount of ammonia formed and from this the percentage of nitrogen in the organic compound.

Calculation.—Let the weight of substance taken = w gm.

Volume of acid taken = x c.c. of N acid solution. Volume of alkali required in the back titration = y c.c. of N NaOH solution.

$\therefore$ volume of acid neutralised by ammonia = $(x-y)$ or r c.c., say, of N acid.

$\therefore$ ammonia liberated = r c.c. of N ammonia.

1000 c.c. N ammonia = 17 gm. of NH_3 or 14 gms. of nitrogen.

$\therefore$ r c.c. N ammonia = $0{\cdot}014 \times r$ gm. of nitrogen.

$$\therefore \text{ percentage of nitrogen} = \frac{0{\cdot}014 \times r \times 100}{w} = \frac{1{\cdot}4r}{w}$$

Example.—0·590 gm. of an organic compound containing nitrogen was decomposed by Kjeldahl's method and distilled with caustic soda—the liberated gas was absorbed in 50 c.c. of N/2 H_2SO_4; after absorption the excess acid was neutralised by 30 c.c. of N/2 caustic soda. Calculate the percentage of nitrogen in compound.

Vol. of acid taken = 50 c.c. N/2 acid = 25 c.c. N acid.

Excess acid = 30 c.c. N/2 alkali = 15 c.c. N alkali.

$\therefore$ acid neutralised by ammonia = (25—15) i.e., 10 c.c. N acid.

$\therefore$ ammonia liberated = 10 c.c. N ammonia.

$$\text{percentage of } N_2 = \frac{0{\cdot}014 \times 10}{0{\cdot}590} \times 100 = 23{\cdot}72.$$

Dumas' method is applicable to all types of nitrogenous organic compounds. But the Kjeldahl's method gives reliable results only with those types of compounds in which *the nitrogen exists in a non-oxidised form*—the method, for example, is unsuitable for the analysis of nitro, nitroso, azo, and azoxy compounds. Cyclic nitrogenous compounds, such as pyridine, cannot be analysed by this method. The method, however, has the merit of being quicker and less laborious, and is largely used in the routine analysis of soil, fertilisers, natural waters, and foodstuffs, etc.

Estimation of other elements.—(a) **Halogens.** The halogens, chlorine, bromine and iodine, are usually estimated by *Carius' method* in which a weighed quantity of the substance is oxidised with fuming nitric acid in presence of a few crystals of silver nitrate in a sealed tube—the tube is placed in an iron case and heated in a special type of furnace, usually at about 200°C, during four hours. Any halogen present is converted into silver halide. The tube is then cooled and carefully opened, and its contents are washed out with distilled water, collected, and weighed as silver halide.

Calculation.—Let the weight of the substance $= w_1$ gm. Weight of AgX formed (where X = Cl, Br or I) $= w_2$ *gm.*

$$\therefore \text{ percentage of X} = \frac{x}{(108+x)} \times \frac{w_2}{w_1} \times 100,$$

where x = atomic weight of X.

Example.—0·3149 gm. of an organic compound containing chlorine gave 0·4025 gm. of silver chloride by analysis by Carius' method. Calculate the percentage of chlorine in the compound.

$$\% \text{ of chlorine} = \frac{35{\cdot}5}{(108+35{\cdot}5)} \times \frac{0{\cdot}4025}{0{\cdot}3149} \times 100 = 31{\cdot}62$$

(b) **Sulphur.**—Sulphur is estimated by Carius' method in much the same way as the halogens. The compound is oxidised by heating with fuming nitric acid in a sealed tube, *but without the addition of silver nitrate.* The resulting sulphuric acid is then precipitated and weighed as barium sulphate.

Example.—0·250 gm. of thiourea gave 0·766 gm. of $BaSO_4$ (mol. wt. 233).

$$\therefore \text{ percentage of sulphur} = \frac{32}{233} \times \frac{0{\cdot}766}{0{\cdot}250} \times 100 = 42{\cdot}07$$

(c) **Phosphorus.**—Under similar conditions as above phosphorus is oxidised by nitric acid to phosphoric acid which may be precipitated as magnesium ammonium phosphate, $MgNH_4PO_4$, and finally weighed in the form of magnesium pyrophosphate, $Mg_2P_2O_7$.

(d) **Oxygen.**—There is no suitable general method for estimating oxygen in organic compounds. The percentage of oxygen is always found out by *difference,* when the percentages of all other elements present in an organic compound are known from analysis.

In numerical problems involving percentage composition, if the sum of the percentages of different elements does not come up to 100, the *deficit* (if considerable) is assumed to be the percentage of oxygen in the substance.

XXIV

EMPIRICAL AND MOLECULAR FORMULAE

Empirical and molecular formulae.—The empirical formula of an organic compound is calculated from its percentage composition, i.e., *from the results of quantitative analysis.* But to find out the molecular formula, the molecular weight of the substance must be known.

Determination of molecular weight by physical methods include:

(a) *Vapour density method*—molecular weights of volatile liquids, e.g., acetone, alcohol, benzene, chloroform, etc., are usually found out by *Victor Meyer's vapour density method* (page 106, part I).

(b) Methods involving measurements of (i) *osmotic pressure,* (ii) *lowering of vapour pressure,* (iii) *elevation of boiling point,* and (iv) *lowering of freezing point, of a solution* (page 108, part I).

The method of arriving at empirical and molecular formulae is explained with reference to a few actual examples.

Example 1.—0·1793 gm. of an organic compound containing C, H, and O only, gave on combustion 0·3586 gm. of CO_2 and 0·1467 gm. of H_2O. Calculate its empirical formula.

The steps in calculation are as follows : (i) Calculate the weights of C and H in the weight of the compound taken :

Weight of carbon = 0·3586×12/44 = 0·0978 gm.
Weight of hydrogen = 0·1467×2/18 = 0·0163 gm.
Weight of substance taken = 0·1793 gm.
0·1141 gm.
∴ Weight of oxygen = 0·0652 gm.

(ii) Divide the weight of each element by its atomic weight :

C = 0·0978/12 = 0·008149
H = 0·0163/1 = 0·0163
O = 0·0652/16 = 0·004075

These numbers are proportional to the number of atoms of each element present in the compound.

In order to avoid cyphers it is convenient to multiply each of the above numbers by 1000. Then, C = 8·149, H = 16·3, and O = 4·075.

(iii) Divide the proportional numbers so obtained by the lowest :

C = 8·149/4·075 = 2; H = 16·3/4·075 = 4;
O = 4·075/4·075 = 1 ∴ empirical formula is C_2H_4O.

Example 2.—0·1886 gm. of an organic compound gave 0·2175 gm. of CO_2 and 0·0222 gm. of H_2O on combustion.

0·1791 gm. of the same substance gave 29·1 c.c. of nitrogen collected over water at 17°C and 743 mm. pressure. Aqueous tension at 17° is 14·5 mm. Calculate the empirical formula.

Weight of carbon = 0·2175×12/44 = 0·05932 gm.
Weight of hydrogen = 0·0222×2/18 = 0·002473 gm.

$$\text{Volume at } N_2 \text{ at N.T.P.} = \frac{29\cdot1\times(743-14\cdot5)\times273}{290\times760} = 26\cdot26 \text{ c.c.}$$

22·4 litre of nitrogen at N.T.P. weighs 28 gm.
0·02626 litre of N_2 at N.T.P. weighs 28×0·02626/22·4 = 0·03283 gm
i.e., 0·1791 gm. of the substance contain 0·03283 gm. of N_2.

$$\therefore \ 0\cdot1886 \text{ gm. ,, ,, ,, } \frac{0\cdot03283\times0\cdot1886}{0\cdot1791}\text{ gm.}$$

i.e., 0·03457 gm. of N_2.

∴ Wt. of C = 0·05932 gm.
Wt. of H = 0·00247 gm.
Wt. of N = 0·03457 gm.
0·0964 gm., nearly.

∴ wt. of O = 0·1886 gm.
0·0964 gm.
0·0922 gm.

Multiplying these numbers by 1000 (in order to avoid cyphers) and dividing by at. wts. of C, etc., we get :

C = 59·32/12 = 4·943; H = 2·47/1 = 2·47;
N = 34·57/14 = 2·470; O = 92·2/16 = 5·762.

Dividing these proportional numbers by the lowest amongst them :

C = 4·943/2·47 = 2; H = 2·47/2·47 = 1 :
N = 2·47/2·47 = 1; O = 5·76/2·47 = 2·33.

Multiplying by 3 to bring to whole numbers :

C = 6 H = 3 N = 3 O = 7
the empirical formula is $C_6H_3N_3O_7$.

Example 3.—An organic compound of molecular weight 60 contains 20·0% C and 6·7% H_2. 0·3 gm. of it gave 112 c.c. of N_2 at N.T.P. Find its molecular formula.

$$\text{Weight of 112 c.c. of } N_2 \text{ at N.T.P.} = \frac{28\times112}{22400} = 0\cdot14 \text{ gm.}$$

∴ percentage of N_2 in the compound = 0·14×100/0·3 = 46·67
∴ percentage of O_2 = 100−(20·0 + 6·7 + 46·67) = 26·63
∴ C = 20%; H = 6·7%; N = 46·67%; O = 26·63%.
Dividing by their respective atomic weights:
C = 1·67; H = 6·7; N = 3·33; O = 1·67.
Dividing by the lowest number 1·67:
C = 1; H = 4; N = 2; O = 1
∴ the empirical formula CON_2H_4.

Let the molecular formula be $(CON_2H_4)n$, then (12+16+28+4)n = 60, whence n = 1. ∴ the molecular formula is CON_2H_4.

Example 4.—1·2 gm. of an organic compound gave on combustion 0·88 gm. of CO_2 and 0·72 gm. of H_2O. On decomposition by Kjeldahl method the same weight of the substance gave ammonia which neutralised 40 c.c. of (N)H_2SO_4.

A 2 per cent aqueous solution of the substance depresses the freezing point of water by 0·62°C (Molar depression of freezing point of water is 1·86).

Calculate the empirical and molecular formula of the substance.

Wt. of carbon = 0·88×12/44 = 0·24; wt. of hydrogen = 0·72×2/18 = 0·08
40 c.c. NH_2SO_4 = 40 c.c. N NH_3 = 0·014×40 = 0·56 gm. N_2
∴ wt. of oxygen = 1·2−(0·24+0·08+0·56) = 0·32 gm.
Dividing by the respective atomic weights:
C = 0·24/12 = 0·02; H_2 = 0·08/1 = 0·08;
N_2 = 0·56/14 = 0·04; O_2 = 0·32/11 = 0·02

Dividing by the lowest number: C = 1, H = 4, N = 2 and O = 1
∴ the empirical formula is CON_2H_4.

Now, $m = K.\frac{a\times1000}{b\times dt}$ (p. 111, part I); ∴ $m = 1·86\times\frac{2\times1000}{100\times0·62} = 60$

Let the molecular formular be $(CON_2H_4)n$.
∴ (12+16+28+4)n = 60, whence n = 1; ∴ molecular formula is CON_2H_4.

Determination of molecular weight by chemical methods.—Chemical methods may be used to determine the molecular weights of organic acids and bases when their *basicity* or *acidity* is known.

(i) **Organic acids.** The molecular weight is given by the relation:
mol. wt. = equivalent wt. × basicity.

The equivalent weight may be determined: **(a) by direct titration** of a weighed quantity of the acid (0·2—0·5 gm.) by standard decinormal NaOH solution, with phenolphthalein as indicator.

Let v c.c. of N NaOH solution = w gm. of the acid.
∴ 1000 c.c. ,, ,, ,, = 1000 w/v gm. ,,
∴ equivalent weight of the acid = 1000 w/v.

(b) by analysis of the silver salt.—A weighed quantity of the silver salt is strongly ignited in a crucible, when a residue of metallic silver remains, which is weighed on cooling.

Let w gm. of silver salt give w_1 gm. of silver as residue.

$$\therefore \frac{\text{Equivalent weight of Ag-salt}}{\text{Equivalent weight of silver}} = \frac{\text{Weight of Ag-salt ignited}}{\text{Weight of Ag residue}}$$

i.e., $\frac{\text{Eq. wt. of Ag-salt}}{108} = \frac{w}{w_1}$ ∴ eq. wt. of Ag-salt $= \frac{w}{w_1}\times108$

Now, the eq. wt. of an acid is the wt. of it which contains 1 equivalent weight of hydrogen replaceable by a metal.

$\therefore$ eq. wt. of acid = eq. wt. of Ag-salt − eq. wt. of silver + eq. wt. of hydrogen $= (\frac{w}{w_1}\times 108-108+1)$.

$$\therefore \text{ mol. wt. of acid} = (\frac{w}{w_1}\times 108-108+1)\times n,$$

where n is the basicity of the acid.

Example.—0·4996 gm. of the silver salt of a dibasic acid gave on ignition 0·2965 gm. of silver. Calculate the molecular weight of the acid.

$$\text{Equivalent weight of the acid} = \frac{0{\cdot}4996}{0{\cdot}2965}\times 108-108+1 = 75$$

$\therefore$ mol. wt. of the acid = 75×2 = 150, since the basicity is 2.

(ii) **Organic bases.**—The molecular weight of an organic base is given by the relation: mol. wt = its equivalent weight × acidity.

Organic bases, e.g., amines form crystalline double salts (chloroplatinates) with chloroplatinic acid, H_2PtCl_6. The chloroplatinates leave a residue of metallic platinum on ignition. Let w gm. of the chloroplatinate of a base give w_1 gm. of platinum. Now, chloroplatinic acid, H_4PtCl_6 (mol. wt. 410) is dibasic and hence its equivalent weight is 205.

410 gm. of chloroplatinic acid contain 195 gm. of platinum (atomic weight 195).

$\therefore$ 205 gm., i.e., one eq. wt. of H_2PtCl_6 contain 195/2 gms. of platinum.

Let the equivalent weight of the base $= x$,

$\therefore$ the eq. wt. of the chloroplatinate $= x+205$.

One equivalent of the chloroplatinate contains 195/2 gms. of plainum.

$$\therefore \frac{\text{eq. wt. of chloroplatinate}}{195/2} = \frac{\text{wt. of chloroplatinate ignited}}{\text{wt. of platinum residue}}$$

$$\text{i.e.,}\quad \frac{x+205}{195/2} = \frac{w}{w_1};\quad \therefore\quad x = \frac{w}{w_1}\times\frac{195}{2}-205$$

$$\therefore \text{ mol wt of the base} = (\frac{w}{w_1}\times\frac{195}{2}-205)\times n,$$

where n is the acidity of the base.

Example.—0·7502 gm. of the chloroplatinate of a diacid organic base left on ignition 0·2078 gm. of platinum. Find the mol. wt. of the base.

Let x = eq. wt. of the base; its acidity is 2.

$$\therefore \frac{x+205}{195/2} = \frac{0{\cdot}7502}{0{\cdot}2078};\quad \therefore\quad x = \frac{0{\cdot}7502}{0{\cdot}2078}\times\frac{195}{2}-205 = 147$$

$\therefore$ the mol. wt. of the base = 147×2 = 294.

EXERCISES

1. 0·2136 gm. of an organic compound gave 0·6012 gm. of CO_2 and 0·0894 gm. of H_2O. What is its empirical formula? $C_{11}H_8O_2$.

2. 0·354 gm. of an organic substance gave on analysis 0·792 gm. of CO_2 and 0·486 gm. of H_2O. The same weight of the substance gave 67·2 c.c. of N_2 at N.T.P. The vapour density of the substance is 29·5. Calculate its molecular formula. *Delhi Inter.* C_3H_9N.

3. 0·6 gm. of an organic compound gave on combustion 1·148 gm. of CO_2

and 0·704 gm. of H_2O. 0·23 gm. of the substance occupied a volume of 112 c.c. at N.T.P. Find its molecular formula. C_2H_6O.

4. 0·15 gm. of an organic liquid gave on combustion 0·33 gm. of CO_2 and 0·18 gm. of water. Its vapour density was 30. Calculate its molecular formula. C_3H_8O.

5. 0·15 gm. of a substance containing nitrogen gave 64·85 c.c. of N_2 measured at 29°C and 756 mm. pressure. Aqueous tension at 29°C is 30 mm. Calculate the percentage of nitrogen in the sample. 46·67%.

6. 0·225 gm. of an organic compound was decomposed by Kjeldahl method and distilled with excess of caustic soda. The liberated ammonia was absorbed in 25 c.c. of NH_2SO_4. After absorption the acid solution was made up to 250 c.c. 25 c.c. of the diluted solution required 20 c.c. of N/10 NaOH for neutralisation. Calculate the percentage of nitrogen in the sample. 31·11%.

7. 0·100 gm. of a monobasic organic acid gave 0·2525 gm. of CO_2 and 0·0432 gm. of H_2O on combustion. 0·122 gm. of the acid was neutralised by 10 c.c. of N/10 alkali. What was the acid? *Punjab Inter.*; C_6H_5COOH.

8. 1·195 gm. of a compound on analysis gave: C 0·12 gm., H 0·01 gm., and Cl 1·065 gm. Its vapour density was 59·75. Find its formula. *Delhi Inter.* $CHCl_3$.

9. 0·185 gm. of an organic compound gave on combustion 0·440 gm. of CO_2 and 0·225 gm. of H_2O. Its vapour density was 37. What is the molecular formula? $C_4H_{10}O$.

10. 0·109 gm. of an organic compound gave on analysis 0·088 gm. of CO_2 and 0·045 gm. of H_2O. 0·185 gm. of it gave 0·319 gm. of AgBr. Find its molecular formula. *Bombay Inter.* C_2H_5Br.

11. 0·354 gm. of an organic substance gave on combustion 0·415 gm. of CO_2 and 0·212 gm. of H_2O. 1·125 gm. of the substance gave enough ammonia by Kjeldahl method to neutralise 30 c.c. N/2 H_2SO_4.

1·47 gm of the substance depressed the freezing point of 175 gm. of benzene by 0·56°. Molar freezing point constant of benzene is 5. Calculate the molecular formula. $C_2H_5NO_2$.

12. A dibasic acid was found to contain 26·70% C and 2·20% H_2, and the rest oxygen. The vapour density of its dimethyl ester was 59. What was the acid? *Punjab Inter*; Oxalic acid, HOOC-COOH.

13. 0·6813 gm. of silver salt of a tribasic acid gave on heating 0·4302 gm. of metallic silver. Calculate the molecular weight of the acid. Mol. wt. 192.

14. The silver salt of an organic acid contained 59·33% of silver. Calculate the equivalent weight of the acid. Eq. wt. 75.

15. 0·6483 gm. of silver salt of a monobasic organic acid gave on ignition 0·2858 gm. of silver. Calculate the molecular weight of the acid. Mol. wt. 138.

16. A monobasic organic acid on analysis gave the empirical formula CH_2O. Its methyl ester had a vapour density of 37. 0·4120 gm. of the silver salt of the acid left 0·2665 gm. of silver on ignition. What was the acid? *Delhi Inter.* CH_3COOH.

17. A dibasic acid containing 26·66% of C and 2·22% of H_2, and the rest oxygen, gave a silver salt contaning 71·05% of silver. What is the formula of the acid? *Bombay Inter.* HOOC-COOH.

18. 0·381 gm. of an organic acid on combustion gave 0·962 gm. of CO_2 and 0·163 gm. of H_2O. 0·428 gm. of silver salt of the acid gave 0·202 gm. of silver on ignition. What is the equivalent weight and formula of the acid? *Delhi Inter.* $C_7H_6O_2$.

19. 0·5025 gm. of the chloroplatinate of an organic base gave on ignition 0·1644 gm. of platinum. Find the equivalent weight of the base. Eq. wt. 93.

20. 0·5435 gm. of the chloroplatinate of a monoacid base left on ignition 0·2120 gm. of platinum. Find the molecular weight of the base. Mol. wt. 45.

QUESTIONS

I

1. Define organic chemistry and historically trace its growth. What are its distinctive features which justify its study as a separate branch of chemistry? *Patna Inter.*

2. (i) Illustrate the characteristics of a homologous series with reference to paraffin hydrocarbons.

(ii) Attempt a classification of the organic compounds according to the functional groups present in them.

(iii) Write notes on the theory of carbon linkage. Illustrate with examples. What are alkyl radicals?

II

3. (i) What are paraffins? Give an account of isomerism among the paraffins.

(ii) Describe with examples: (a) Wurtz reaction, (b) Kolbe's synthesis, (c) Grignard's reaction.

4. (i) Outline the synthesis of methane and ethane, starting with: (a) acetic acid, and (b) methyl alcohol.

(ii) Explain the statement that methane is a saturated hydrocarbon.

5. An organic compound (A) containing 8·45% C, 2·12% H_2 and 89·43% iodine, gave on reduction a hydrocarbon which was also formed by heating sodium acetate with soda lime. Also on treatment with sodium in presence of ether A gave a hydrocarbon which was identical with that obtained by electrolysis of sodium acetate. What was A and what were the hydrocarbons formed?

Methylodide, CH_3I; *methane*, CH_4; *ethane*, CH_3-CH_3.

III

6. (i) Explain the terms: double bond, triple bond. How would you detect the presence of unsaturation in an organic compound?

(ii) Compare the properties of ethylene and ethane. How would you separate a mixture of ethylene and ethane.

(iii) Mention the tests for distinguishing between the following gases: methane, ethylene, acetylene, carbon monoxide, and hydrogen.

7. (i) Starting with ethylene, outline the steps for obtaining: acetylene, ethyl alcohol, glycol, and ethane.

(ii) Given acetylene, how would you prepare: ethylene, ethyl alcohol, acetic acid, and benzene.

8. Explan what hapenns when: (a) ethylene is passed into bromine, and the product formed is treated with alcoholic potash, (b) acetylene is treated with hydriodic acid, (c) acetylene is led into hot dilute sulphuric acid containing mercuric sulphate, (d) ethylene bromide s heated with zinc dust, (e) ethylene is treated with ozonised oxygen and the product formed is treated with water.

9. An olefinic hydrocarbon: (i) gives propane on catalytic hydrogenation, (ii) adds HI to form a compound which on treatment with moist silver oxide gives an alcohol, which on oxidation gives acetone. What is the hydrocarbon?

Propylene, CH_3-$CH = CH_2$.

10. An olefine gives two molecules of formaldehyde on ozonolysis. What is the hydrocarbon? *Ethylene*, $CH_2 = CH_2$.

11. A and B are two olefinic hydrocarbons of tho same forlmula C_4H_8. On oxidation with excess of $KMnO_4$, A gives 2 molecules of acetic acid, and B gives propionic acid and CO_2. What are A and B?

A, CH_3-$CH = CH$-CH_3; B, CH_3-CH_2-$CH = CH_2$.

12. An unsaturated hydrocarbon, A, containing 90% C and 10% H_2, had a mol. wt. of 40. It reacted with ammoniacal cuprous chloride solution, and gave acetone on hydration in presence of $HgSO_4$ and dilute H_2SO_4. What was A?

Methyl acetylene, CH_3-$C{\equiv}CH$.

13. An organic compound (vapour density 14) gave on analysis 85·7% C and 14·3% H_2. It decolorised bromine water, and reacted with ozone, forming an ozonide which on hydrolysis gave formaldehyde. What was the compound?

Ethylene, $CH_2 = CH_2$.

IV

14. Describe the preparation of ethyl iodide, and mention its synthetic uses. *Bombay Inter.*

15. (i) How is chloroform prepared and what are its important properties? What precautions are taken to store it and why? Mention its uses.

Patna Inter.

(ii) How would you test the purity of a sample of chloroform?

16. (i) How would you distinguish between ethylene chloride and ethylidene chloride?

(ii) What hydrocarbons are formed by the action of sodium on a mixture of methyl and ethyl iodides?

(iii) Describe the action of alcoholic potash on: (a) chloroform, (b) ethyl bromide, and (c) ethylene bromide.

(iv) Outline the steps for conversion of methane into acetic acid and *vice versa.*

(v) Describe the action of bleaching powder on ethyl alcohol or acetone.

17. (i) Given a sample of ethyl iodide, how would you obtain: (a) ethane, (b) glycol, (c) propionic acid, (d) ethyl amine, (e) acetaldehyde, and (f) n-butane.

(ii) Describe a haloform reaction with examples.

18. An organic liquid gave on analysis 10·06% C, 0·84% H_2 and 89·1% chlorine. Its vapour density was 60. It gave carbylamine reaction. What was the liquid? *Chloroform,* $CHCl_3$.

V

19. What are primary, secondary, and tertiary alcohols? How are they distinguished from one another? How can methyl alcohol be converted into ethyl alcohol? *Nagpur Inter.*

20. What is pyroligneous acid and how is it obtained? What simple compounds does it contain and how are they separated? *Patna Inter.*

21. (i) How would you introduce an -OH group in organic compound? How can you detect the presence of such a group?

(ii) Starting from ethyl alcohol, how would you obtain: methane, ethane, ethylene, acetylene, acetic acid, diethyl ether, and ethyl amine?

(iii) Describe the action of: sodium, acetyl chloride, phosphorus pentachloride, chlorine, and nitric acid upon ethyl alcohol.

(iv) How would you separate acetic acid from ethyl alcohol?

22. What is alcoholic fermentation? How is it used in making ethyl alcohol from starch? How is ethyl alcohol distinguished from methyl alcohol? *Nagpur Inter.*

23. An organic compound (b.p. 78°) gave on analysis 52·2% C and 13·04% H_2. Its vapour density was 23. It gave acetaldehyde on careful oxidation, and also responded to the iodoform reaction. What was the compound. *Ethyl alcohol,* CH_3CH_2OH.

24. Two isomeric organic compounds contain 52·18% C, 13·1% H_2, and the rest oxygen. One of the isomers reacts with sodium, and the other does not. What are the compounds? Suggest their structural formulae. *Ethyl alcohol,* C_2H_5OH; *Dimethyl ether,* CH_3-O-CH_3.

25. An organic liquid, A, (vapour density 30) was found to contain 60% C, 13·33% H_2. On dehydration it gave an olefine (of the formula C_3H_6) which dissolved in cold concentrated sulphuric acid. The solution on dilution and boiling gave a liquid, B, which was isomeric with the original liquid. What were A and B? *n-propyl alcohol,* $CH_3CH_2CH_2OH$, and *secondary propyl alcohol,* CH_3-CHOH-CH_3.

VI

26. Write the names and structural formulae for two compounds represented by the molecular formula C_2H_6O. By what characteristic reactions can they be identified? What kind of relationship exists in such class of compounds? *Nagpur Inter.*

27. Describe the preparation of di-ethyl ether from ethyl alcohol by 'continuous etherification process'. Discuss the 'continuous' nature of the reaction. Mention the important properties and uses of ether. *Bihar Inter.*

28. (a) Which *ethers* correspond to the formula $C_4H_{10}O$? How would you establish their identity? What is meant by metamerism?

(b) What different compounds can you obtain from ethyl alcohol and sulphuric acid by variation of experimental conditions?

29. A volatile organic liquid (mol. wt. 74) was found to contain 64·86% C and 13·38% H_2. Sodium had no action upon it, but on being heated with HI it gave an alkyl iodide (b.p. 72°) containing 81·4% iodine. What was the liquid? Diethyl ether, C_2H_5-O-C_2H_5.

VII

30. Describe the preparation of acetaldehyde and acetone from acetic acid. Compare the chemical properties of acetaldehyde and acetone. *Bombay Inter.*

31. (a) By what practical tests would you distinguish between acetaldehyde, acetone and ethyl alcohol? (b) Explain what happens when; (i) acetaldehyde is treated with potassium carbonate solution; (ii) strong sulphuric acid is added to acetone; (iii) formaldehyde is treated with ammonia; (iv) acetaldehyde is treated with ethyl alcohol in presence of HCl gas; (v) formalin is boild with a strong solution of caustic soda; (vi) calcium acetate is strongly heated alone, and in presence of calcium formate.

32. How would you prepare: (i) acetaldehyde from acetylene, (ii) urotropin from methanol, (iii) acetone from ethyl alcohol, (iv) chloroform from acetone, (v) chloral from ethanol?

33. (i) Mention the typical reaction of the carbonyl group, $>CO$, as shown by the chemical properties of acetaldehyde and acetone.

(ii) Indicate the tests for distinguishing formaldehyde and actaldehyde.

(iii) What is the essential difference between condensation and polymerisation? Illustrate wth xamples.

34. What is acetone? How is it prepared? Compare and contrast the properties of acetone with those of acetaldehyde. *Nagpur Inter.*

35. On dry distillation of calcium acetate a liquid was obtained which: (a) was found to contain 62·07% C, and 10·34% H_2; (b) had a vapour density of 29; (c) gave positive iodoform reaction, but did not reduce ammoniacal silver nitrate solution. Identify the liquid. *Acetone*, CH_3-CO-CH_3

36. An organic compound was found to contain 40% C and 6·6% hydrogen. Its vapour density was 15. It restored the colour of Schiff's reagent and gave on oxidation an acid which evolved CO on being treated with conc. H_2SO_4. The original compound as well as its oxidation product reduced silver nitrate solution. What was the compound. *Formaldehyde*, HCHO.

37. An organic compound (vapour density 22) was found to contain 54·54% C and 9·09% H_2. It restored the colour of Schiff's reagent, and with hydroxylamine gave an oxime which contained 23·3% of nitrogen. On oxidation it formed a compound of mol. wt. 60. What was the compound? *Acetaldehyde*, CH_3CHO.

38. An organic liquid (vapour density 29) was found to contain 62·06% C and 10·35% H_2. It gave a positive iodoform reaction, and an oxime with hydroxylamine. On reduction it gave an alcohol which on dehydration formed an olefine, C_3H_6. The olefine gave acetaldehyde and formaldehyde on ozonolysis. What was the liquid. *Acetone.*

VIII

39. How is acetic acid prepared? Give its uses. Starting with acetic acid how would you obtain: acetic anhydride, acetamide, and amino-acetic acid? *Poona Inter.*

40. How is formic acid prepared in the laboratory. Describe its properties, and compare its chemical behaviour with that of acetic acid. *U. P. Board, Inter.*

41. Describe the 'quick vinegar' process for making acetic acid. Starting from acetic acid, how would you obtain: formic acid, acetone, and methyl alcohol? *Nagpur Inter.*

42. (i) Outline a method for the synthesis of acetic acid.

(ii) How would you make: (a) formic acid from oxalic acid, (b) oxalic acid from formic acid?

(iii) Mention tests for distinguishing formaldehyde, formic acid and acetic acid.

43. (i) Explain what happens when acetic acid is treated with: chlorine, PCl_5, $SOCl_2$ and ethyl alcohol.

(ii) Starting with acetic acid how would prepare: methane, ethane, and ethyl alcohol?

4. Two organic compounds, A and B, have the same molecular formula $C_2H_4O_2$. On treatment with sodium bicarbonate in the cold A remains unchanged, while B reacts evolving CO_2. On hydrolysis with aqueous caustic soda A gives: (a) an alcohol which does not give iodoform reaction, and (b) a sodium salt

of an acid which decolorises warm $KMnO_4$ solution acidified with dilute H_2SO_4, and evolves CO when treated with conc. H_2SO_4. Identify A and B.

A, methyl formate, $HCOOCH_3$, and *B, acetic acid*, CH_3COOH.

45. An organic liquid, A, was found to contain 52·17% C and 13·04% H_2. It gave a positive iodoform reaction, and formed an acid liquid, B, (empirical formula, CH_2O) on oxidation. A and B reacted in presence of conc. H_2SO_4 to give a liquid, C. C had a fruity smell and contained 54·54% C, 9·1% H_2 and the rest oxygen. The bol. wt. of C was 88. Identify A, B, and C.

A, ethyl alcohol, C_2H_5OH; *B, acetic acid*, CH_3COOH; C. *ethylacetate*, $CH_3COOC_2H_5$.

IX

46. (a) How is acetyl chloride prepared? What is the action of water, ethyl alcohol, and ammonia on acetyl chloride? *U. P. Board, Inter.*

(b) Show how acetyl chloride is used for the introduction of an acetyl radical, CH_3-CO-, in an organic compound.

47. How is ethyl acetate prepared in the laboratory? How does it react with: (a) ammonia, (b) sodium and alcohol, (c) methyl alcohol, (d) aqueous caustic soda, (d) phosphorus penta chloride?

48. (i) Describe the action of: (a) aqueous caustic soda, (b) bromine and caustic potash, (c) phosphorus pentoxide, on the product obtained by heating ammonium acetate.

(ii) How is acetic acid converted into: (a) acetamide, (b) acetic anhydride, and (c) acetonitrile, and (d) glycine.

49. 0·180 gm. of an organic compound gave 0·264 gm. of CO_2 and 0·108 gm. H_2O. Its vapour density was 30.

On boiling with NaOH solution, it gave methyl alcohol and sodium salt of an acid. What is its molecular formula? Give its structural formula and name it. *Bombay Inter. Methyl formate*, $HCOOCH_3$.

50. 0·88 gm. of an organic liquid gave on analysis 54·54% C and 9·09% H_2. Its mol. wt. was 88. On hydrolysis with aqueous NaOH, it gave: (a) sodium salt of an acid which on distillation with soda lime gave methane; (b) a volatile product which gave iodoform reaction, and formed a substance on oxidation which reduced Fehling's solution. *Ethyl acetate*, $CH_3COOC_2H_5$.

51. 0·27 gm. of an organic substance gave 0·4023 gm. of CO_2 and 0·2061 gm. of H_2O on analysis. 0·24 gm. of the same substance gave 45·6 c.c. of dry nitrogen at N.T.P. Find its empirical formula. Hydrolysis of the substance yielded an ammonium salt, while an alkyl cyanide was formed on heating the substance with P_2O_5. Identify the substance. *Acetamide*, CH_3CONH_2.

52. An organic liquid (mol. wt. 41) contained 58·53% C, 7·31% H_2 and the rest nitrogen. On hydrolysis with hot dilute H_2SO_4, it gave a monobasic acid whose: (a) silver salt contained 64·67% silver, and (b) ethyl ester had a vapour density of 44. On reduction it gave a monoacid organic base which reacted with nitrous acid, giving ethyl alcohol and nitrogen. What was the liquid?

Methyl cyanide, CH_3CN.

53. A nitrogeneous organic solid contained 40·67% C, and 8·47% H_2. 0·59 gm. of the substance gave sufficient ammonia by Kjeldahl method to neutralise 10 c.c. NH_2SO_4. On hydrolysis with hot aqueous alkali, it gave NH_3, and a salt of an acid which formed methane on being heated with soda lime. The original compound also reacted with nitrous acid, evolving N_2. *Acetamide*, CH_3CONH_2.

X

54. (i) What are fats, oils and waxes? Illustrate with examples.

(ii) Outline a process for the hydrogenation of oils. Why does butter fat gets rancid?

(iii) What is meant by saponification of oils?

55. (i) What is glycerol? To what class of compounds does it belong? How is it prepared on a large scale? Mention its important uses. *Nagpur Inter.*

(i) How is nitroglycerine prepared? What are its uses?

XI

56. Outline the various methods for the preparation of a primary amine. How is a primary amine distinguished from a secondary and a tertiary amine. *Nagpur Inter.*

57. (i) Distinguish clearly between : (a) acetamide and methyl amine, (b) ammonia and methyl amine, (c) ammonium hydroxide and tetramethyl ammonnium hydroxide.

(ii) What is carbylamine reaction? Illustrate.

(iii) Describe the action HNO_2 on acetamide and ethyl amine.

58. Outline the processes to prepare : (a) ethyl alcohol from methyl alcohol, (b) formic acid from acetic acid, (c) methyl amine from acetic acid, (d) ethyl amine from acetic acid.

59. An organic liquid, A has the empirical formula C_2H_7N. It reacts with HNO_2, evolving N_2 and forming a neutral liquid B. B reacts with sodium, giving off H_2, and also gives iodoform reaction. A, *ethyl amine*, $C_2H_5NH_2$; B, *ethyl alcohol*, C_2H_5OH.

60. An organic compound, A, contained 53·33% C, 15·55% H_2. It reacted with HNO_2, giving an alcohol and N_2. The alcohol contained 52·17% C and 13·04% H_2 and gave on careful oxidation a compound, B, which restored the colour of Schiff's reagent and also reduced Fehling's solution. What were A and B?

A, ethyl amine, $C_2H_5NH_2$; *B, ethyl alcohol*, C_2H_5OH.

XII

61. What are the sources of oxalic acid? How is it made commercially? Describe the action of : (i) heat, (ii) concentrated sulphuric acid, (iii) $KMnO_4$ solution acidified with dilute H_2SO_4, (iv) phosphorus pentachloride, (v) ethyl alcohol, on oxalic acid.

62. What is urea? How is it prepared? What are its uses? Describe the action of : (i) nitrous acid, (ii) nitric acid, (iii) caustic soda and (iv) sodium hypobromite, upon urea.

63. (i) How would you prepare : (o) oxalic acid from cane sugar, (b) succinic acid from ethyl alcohol, (c) malonic acid from acetic acid, (d) acetic acid from malonic acid.

(ii) What is biuret reaction?

(iii) How would you estimate the percentage of urea in a sample of urine?

XIII

64. (i) What is the source of lactic acid? How is it prepared? Outline the synthesis of lactic acid from ethyl alcohol. Describe the action of : (a) heat, (b) sulphuric acid, (c) ethyl alcohol, and (d) hydrogen peroxide upon lactic acid.

(ii) What is optical activity? Discuss the stereoisomerism of lactic acid. Why is sour milk lactic acid optically inactive?

65. Describe the preparation, properties, and uses of tartaric acid. How would you detect a tartrate and distinguish it from a citrate and an oxalate?

6. How many tartaric acids are known? How could you account for the existence of various forms of tartaric acid?

67. (i) Outline a synthesis of tartaric acid, starting with ethylene.

(ii) How would you convert acetic acid into glycolic acid and *vice versa*. *Punjab Inter.*

(iii) Outline the preparation of citric acid from lemon juice.

XIV

68. What are carbohydrates? How are they classified? Give illustrations.

69. How is glucose prepared from : (i) starch, (ii) cane sugar? Explain its reactions with Fehling's solution, ammoniacal silver nitrate and hydrazine. Are these reactions also given by fructose? *Punjab Inter.*

70. How is cane sugar extracted from the sugar cane juice? What are the actions of : : (a) concentrated HNO_3, (b) concentrated H_2SO_4, and (c) Fehling's solution, on cane sugar? *E. Punjab Inter.*

71. (i) What is meant by the inversion of cane sugar?

(ii) Suggest tests for distinguishing between glucose, starch, and cane sugar.

(iii) How is glucose converted into fructose?

(iv) Indicate the use of phenyl hydrazine as a reagent in the study of carbohydrates.

XV—XVIII

72a. What is the action of : (a) concentrated nitric acid, (b) bromine, (c) hydrogen in presence of catalyst, (d) hot concentrated sulphuric acid, on benzene and methane? How would you obtain phenol from any of the reaction products? *Calcutta* 1959.

72. What are the important differences between aliphatic and aromatic compounds? Illustrate your answer by reference to methane, ethylene and benzene.

73. (i) Describe the separation of benzene from coal tar. How can benzene be converted into toluene and resorcinol? *Poona Inter*

(ii) Name the common impurities in coal-tar benzene. How would you remove them to get pure benzene?

74. (i) Outline the steps for the conversion of benzene into toluene, and *vice versa*.

(ii) Describe the action of chlorine on toluene.

(iii) Explain with examples the difference between *nuclear* and *side-chain* derivatives of toluene.

75. (i) Writes notes on: (a) Fittig's synthesis, (b) Friedel-Crafts reaction.

(ii) How would distinguish between chlorotoluene and benzyl chloride, both having the molecular formula C_7H_7Cl.

(iii) Explain what happens when: (a) benzoic acid is heated with soda lime, (b) benzyl chloride is heated with alkaline $KMnO_4$ solution, (c) benzotrichloride is boiled with milk of lime, (d) benzene is treated with acetyl chloride in presence of anhydrous $AlCl_3$.

76. 0·25 gm. of a hydrocarbon gave on analysis 0·837 gm. of CO_2 and 0·1955 gm. of H_2O. Its vapour density was 46. On oxidation it yields an acid of the formula $C_7H_6O_2$. The acid gave benzene on distillation with soda lime. What was the hydrocarbon? *Toluene*, C_6H_5-CH_3.

77. An aromatic organic liquid containing 52·2% C, 3·7% H_2 and the rest chlorine, gave on oxidation with alkaline $KMnO_4$, a monobasic acid which formed benzene on being heated with soda lime. What was the liquid?

Benzal chloride, C_6H_5-$CHCl_2$.

78. An aromatic hydrocarbon A, on treatment with methyl chloride in presence of anhydrous $AlCl_3$ gave a hydrocarbon, B, (mol. wt. 92) containing 91·3% carbon and the rest hydrogen. B on oxidation gave a monobasic acid, which gave back A on heating with sodalime. What were A and B?

Benzene, C_6H_6, and *toluene*, C_6H_5-CH_3.

79. How is nitrobenzene prepared? What are its uses? What products does it give on reduction under various experimental conditions?

80. (i) How is aniline prepared in the laboratory? *Annamalai Inter.*

(ii) What reactions take place between aniline and (a) sulphuric acid, (b) glacial acetic acid, (c) benzoyl chloride, (d) chloroform and alcoholic potash, (e) methyl iodide?

(iii) Give an account of the process of steam distillation, and explain the principles upon which it is based.

81. (i) Describe the action of nitrous acid upon amines.

(ii) What are the tests for a primary amine? How would you distinguish between primary aliphatic and aromatic amines?

(iii) How would you *conveniently* obtain ethyl amine from ethyl iodide?

82. (i) Write notes on : (i) diazo reaction, (b) Sandmeyer's reaction, (c) carbylamine reaction.

(ii) Suggest methods for the introduction of the following radicals: OH, NH_2, I, CN, COOH, CH_3, NO_2, and SO_3H, into the benzene nucleus.

(iii) Outline the steps for the conversion of : : (a) benzene into aniline, and *vice versa;* (b) phenol into benzene, and *vice versa;* (c) benzene into benzoic acid, and back.

83. (i) Describe the preparation of acetanilide. What are its uses? How would you obtain aniline from acetanilide? How would you prepare to o-nitroanilines from aniline?

(ii) How is benzene diazonium chloride formed? Describe its reaction with: hot water, ethyl alcohol, KI, and stannous cmhloride.

84. An aromatic hydrocarbon, A, on treatment with conc. HNO_3 gave a compound, B, containing 58·5% C, 4·1% H, and 11·4% N_2. B on reduction gave a monoacid base, C, which gave a carbylamine reaction. What were A, B, and C? *Benzene, nitrobenzene, and aniline.*

XIX—XXIII

85. (i) How is phenol isolated from the middle oil fraction of coal tar? How can you obtain from phenol : (a) salicylaldehyde, and (b) o-hydroxy benzoic acid.
E. Punjab Inter.

(ii) Compare and contrast the chemical properties of : (a) benzyl alcohol and phenol, (b) ethyl alcohol and phenol.

86. Outline the methods for the conversion of benzene into phenol. Mention the properties, tests and uses of phenol.

87. (i) How would you separate a mixture of : (a) phenol and aniline, (b) phenol and benzoic acid?

(ii) Write notes on : *Schotten-Baumann* reaction.

88. Give an account of the occurrence and preparation of benzaldehyde. Compare and contrast its properties with those of acetaldehyde. Mention its important uses. *E. Punjab Inter.*

89. (i) Outline different methods for obtaining benzaldehyde from toluene.

(ii) By what tests would you distinguish between benzaldehyde and acetaldehyde?

90. (i) How does benzaldehyde react with : strong caustic alkali, alcoholic KCN solution, nitric acid, and ammonia? What happens when benzaldehyde is kept exposed to air?

(ii) Writes notes on Cannizzaro's reaction. How would you obtain benzene from acetophenone?

91. (i) How is benzoic acid prepared? Compare its chemical properties with those of acetic acid.

(ii) How is benzoyl chloride prepared? How does it react with : (a) aniline, (b) phenol, (c) sodium benzoate, and (d) ammonia?

92. (i) How is salicylic acid prepared? Mention its properties, tests and uses.

(ii) How is salicylic acid converted into : (a) oil of wintergreen, (b) aspirin?

93. (i) Write notes on : (a) Kolbe's reaction, (b) benzoylation.

(ii) How would you obtain benzene from salicylic acid and *vice versa.*

94. An organic compound (A), $C_7H_6O_3$, on being heated with sodalime gave another compound, B. Both A and B gave violet colour with ferric chloride solution. B possessed a strong phenolic odour and contained 76·60% C, 6·38% H, and the rest oxygen, and also gave benzene on distillation with zinc dust. What were A and B? *Salicylic acid*, $C_6H_4(OH)COOH$, and *phenol*, C_6H_5OH.

95. A nitrogeneous organic compound, A, was found to contain 69·42% C, and 5·78% H.. 0·121 gm. of the substance gave on hydrolysis with hot aqueous alkali ammonia which was neutralised by 10 c.c. of N/10 H_2SO_4. The resulting alkaline solution on being acidified gave a white crystalline precipitate of an acid, which formed benzene on heating with sodalime. What was A.
Benzamide, $C_6H_5\text{-}CONH_2$.

96. Attempt a classification of foods according to their functions. Explain what is meant by the energy value of food. What is meant by a balanced diet?

98. (i) What methods would you employ to obtain an organic liquid in a pure state? How would you test its purity?

(ii) How would you separate a mixture of two liquids having boiling points very near to each other?

(iii) What is meant by '*extraction with ether*'? How is it employed in the purification of organic liquids?

(iv) What are the criteria of purity of an organic substance? You are given two organic compounds, a solid and a volatile liquid. How would you test their purity? If impure, what methods would you employ to purify them?
Patna Inter.

99. How would you detect the presence of nitrogen, sulphur, and chlorine in an organic compound? Give experimental details. *Patna Inter.*

100. Describe methods for the estimation of (a) carbon and hydrogen, (b) nitrogen, in an organic compound.

101. (i) How would you conveniently estimate nitrogen in a given fertiliser?

(ii) How would you infer the presence of oxygen in an organic compound?

Index to Part I Inorganic Chemistry

absolute temp. 65
acetylene 335
acid 36, 131
arsenious 367
arsenic 367
boric (boracic) 374
bromic 286
carbonic 324
chloric 284
chlorauric 468
chromic 488
graphitic 318
hydrazoic 239
hydrobormic 277
hydrochloric 273
hydrocyanic 337
hydroiodic 279
hydrofluoric 261
hydrofluosilicic 380
hypobromous 286
hypochlorous 281
hypoiodous 286
hyponitrous 247
hypophosphorous 364
iodic 287
mellitic 318
muriatic 273
nitric 248, fuming 249
nitrous 246
nitroso sulphuric 307
perchloric 285
periodic 287
persulphuric 213
phosphoric 361
phosphorous 364
prussic 337
pyroligneous 319
pyrosulphuric 307
  -silicic 379
sulphuric 307
  fuming 312
  sulphurous 304
acidity 132
active mass 116
  -nitrogen 221
affinity 26, 117
agate 378
air, 222, liquid 177, 496
  -oven 56
alabaster 419
alkali 39, 176
  caustic 393, mild 394
  -metal 393
  -waste 297, 401
alkaline earth 411
alclad 437
alchemy 5
allegheny 476
allotropy 207, alloy 389
alpha particles 160

aludel 272
alumina 437, -gel 438
aluminium 433
  -bronze 437
alnico 437
aluminoferric 439
  -thermic 436
alum 439, -stone 440
  -shale 440, Roman 440
alundum 438
alunite 433, 440
amalgam 389
amatol 237
amethyst 378
ammonia 228
  -soda process 402
ammoniacal liquor 231,342
ammonium salt 236
  -persulphate 213
  -dichromate 489
  -alum 440
amphoteric oxide 176
amorphous 52
analysis 60
anhydrite 415
anglesite 446
animal charcoal 319
anion & anode 121
annealing 383
anthracite 321
antichlor 216, 316
antifriction metal 369
antimony 369
apatite 415
aqua regia 249
  -fortis 248
aragonite 415
argentite 461
argentum 24
argon 497
Arrhenius 122
arsenic 366
  white 366, 367
arsine 367
arsenical pyrite 366
asbestos 379, 412
atacamite 453
atmolysis 70
atmosphere 222
atomic heat 98
  -number 154, 170
  -structure 152
  -theory 79, 160
  -volume 167
  -weight 22, 87, 97
atomicity 25, 84, 87
atom 22, 79, 83
aurum 24
aurous chloride 470
auric chloride 469

available chlorine, 282
Avogadro's hypothesis 82, 83
  -number 87, 101
azide 242, azote 224
azurite 453
barium 419, baryta 420
barytes 419
Bayer process 434
babbit metal 443
bases 38, 131
basicity 132
basic oxide 175
bauxite 433
Beckmann 111
Baeyer test 335
bell metal 457
beryl 379
Bessemer process 475
beta rays 160
Betts process 448
bicarbonate 393
Birkeland-Eyde 254
bismuth 370
  -ochre, -spar 370
  -glance 370
bismuthite 370
bismuthinite 370
bismuthine 370
bituminous coal 321
bittern 267, 406
black ash 401, -lead 318, -Jack 421
blanc-fixe 213, 420
blast furnace 387, 471
bleaching powder 281
blende 421
blister copper 455
bloom 472
blue vitriol 459
boiling point 9, 112
bone ash 353
  -black, -charcoal 319
boracite 373
Bordeaux mixture 460
borax 375
borocalcite 373
boron 373, bort 318
boiler scale 193
boric acid 374
  -water 193
B. O. V. 308
Boyle's law 64
brass 457
braunite 490
Bredig method 148
brimstone 296
Brin process 178
brine 406
Britannia metal 369

B. Th. U. 340
bromine 267
bronze 457
Brownian motion 149
brown haematite 470
brochantite 453
Bunsen flame 350
butter of tin 445
cadmium 427
cadmiopone 428
calamine 419
calcorani 296
calcite 415
calcination 386
calcium 415
  -carbide 345
  -cyanamide 236
calgon 192, 363
caliche 271
calomel 430, calx 6
calorific value 340
calorising 437
candle flame 348
Cannizzaro 84, 87
carat 316, 468
carbide 345
carbon 317
  -disulphide 345
  -tetrachloride 346
  -dioxide 322
  -monoxide 327
carbonado 318
carbonate 325, 392
carbonyl chloride 328
carbonisation 340
carbonundum 379
carnallite 407, 408
case hardening 475
cassiterite 441
cast iron 472
Castner process 395
  -Kellner cell 398
cat's eye 378
catalysis 145
catalyst 145, 173
cataphoresis 150
cathode 121, -rays 152
cation 121
caustic alkali 397
  -soda 398
  -potash 408
causticising 399
celestine 419
cement 417
  -hydraulic 417
  -portland 417
cementite 472
cementation 475
cerrusite 446
chalcocite 453
chalcopyrite 453
chalk 415
chalybcatewater 189
chamber acid 309
  -crystal 309
charcoals 319 -active 320
Charles' law 64
chemical change 9, 22
  -combination, law of 75
chemiluminescence 348
Chile salt petre 219
china clay 433
chloramine process 194
chlorine 262
chlorapatite 353
chlorargyrite 461
chloride of lime 281
chlorides 390
chrome alum 488
  -green 487
  -red, etc. 489
  -iron stone 486
chromite 486
chromate 488
chromium 486
chromyl chloride 489
chrysoberyl 433
chryso-colla 453
cinnabar 428
Clark process 190
clay 377, 433
clevite 496
coagulation 150
coal 321, -gas 340
cobalt, -glance 482
cobaltite 482
cochrome 482
coinage metal 164
co-ionic bond 158
coke 321
cold flame 355
colemanite 373
colloids 146
  -protective 150
combining capacity 26
  -weight 79
combustion 174, 225, 346
heat of- 142
reciprocal- 346
common salt 406
  -ion effect 137
complex salt 133
compound 17
  -radical 28
  concrete 418
  reinforced- 418
constant proportion, law of 75
conservation of mass, law 12
  -energy 15
coordinate link 158
copper, -pyrite, 453
  -glance 453
  -sulphate 459
copperas 480
coprolite 353
corrosion 476
corrosive sublimate 431
corundum 493
coulomb 124
covalency 157
cristobalite 378
crocoisite 446
crucible 16
cry of tin 443
cryolite 258, 433
cryoscopic constant 111
crystal 52
crystallisation 52
  water of- 55
crystalloid 146
cupellation, cupel 462
cuprite 453
cuprum 24
cyanogen 337
cyanamide 234
dative covalency 158
Davy lamp 347
Dalton's at. theory 79
decantation 41
Deacon process 267
decomposition 60, 128
degree of dissociation 119
deliquescence 57
delta metal 457
density 66, 85, 497
desilverisation 448
detinning 445
desiccator 58
deuterium 159
Dewar flask 177
Devarda's alloy 251
dialysis 147
diamond 317
diaspore 433
diaphragm cell 399
dichromate 488
diffusion 68
displacement 60
dissociation 127
distillation 47-51, -distructive 51
distilled water 48, 195
Dippel oil 319
Dobereiner triad 161
double bond 29
  -decomposition 60
dolomite 412
dry ice 325
Dulong-Petit law 98
duralumin 437
duriron 476
Duplex process 475
Dutch liquid 334
dynamite 249

earth alkaline 411
earthen ware 36
efflorescence 36
effusion 70
electric calamine 421
electro chemical series 130
  -equivalent 125
electroplating 129
  -typing 129
electrode 121
electrolysis 121
electrolyte 121, 122
electrolytic dissociation 122
electron 152, 413
electro valency 156
electro valency 156
  -phoresis 150
  osmosis 150
element 16, 162
elixer of life 5
elevation of b.p. 112
emerald 433
emulsion 47
emery 437
empirical formula 502
enamel 383
endo thermic change 15
energy 15, enzyme 146
Epsom salt 415
equilibrium constant 116
  chemical—115
equivalent wt. 90, 126, 523
  -proportion, law of- 78
ethylene 333
etching 262
euchlorine 285
eudiometry 514
eutectic mixture 47
evaporation 40
exothermic change 15
explosion 346
extraction 59
F. Faraday 126
Faraday's laws 124
Fehling's soln. 457
felspar 377, 433
fero-chrome 486
  -manganese 490
feeri alum 480
ferrum 24, ferrite 478
festel metal 482
ferrous sulphate 480
ferric chloride 479
fire clay 384
  -brick 384
  -damp 330
  -extinguisher 325
fixation of N_2 227
fixed air 322
fineness 464, 468
fixing 465
filtration 41
flame, candle 348
  Bunsen- 350
flint 378, -glass 381
floatation 386
flowers of sulphur 296
fluorapatite 353
fluorine 258
fluorspar 258, 415
flux 387, foamite, 325
formula 24, 28, 502
fountain expt. 229, 274
franklinite 421
Frary metal 449
Frasch process 296
Fremy's salt 259
freezing point 9, 111
  -mixture 46
fractional distillation 49
  -crystallisation 54
fuel 340, furnace 387
fuller's earth 384
fulminating gold 469
  -silver 465
  -nitric acid 249
fuming sulphuric acid 312
fusion mixture 408
galena 446
galvanisation 424
gangue 386
Gay Lussac law 81
  -tower 309
gamma rays 160
garnierite 483
garnet 379
gas 8, -laws 64
  -constant 65
  -carbon 321, 323
  -lime 343, -sylvestre 322
electrolytic- 196
gaseous vol., law of- 81
gel 148
german silver 457
gibbsite 433
glass 380-383
  etching of 262
  annealing of- 383
Glauber salt 406
glaze 384
Glover tower 308
gold 467
Goldschmidt process 436
Gosage method 399
Graham's law 68
gram molecule 25, 100
  -atom 97
gram molecular wt. 25, 100
  -volume 86, 100
graphite 318
greenockite 427
Grignard reaction 332
grinding 386
green vitriol 480
Guignet green 487
gun metal 457, -cotton 249
  -powder 43, 409
gypsum 415
Haber process 232
haematite 470
halogens 258
hydracids 273
hardness of water 189
Hardy-Schultze rule 150
hardening of steel 475
hausmannite 490
hearth 387, 471
heat of formation 142
  -solution 143
  -neutralisation 143
heavy hydrogen 159
  -water 156
  -spar 419
helium 497
Henry's law 62
hepatic water 189
Hess's law 143
heterogeneous body 20
homogeneous body 20
Hoope's process 437
horn silver 461
hydrargyrum 24
hydrate 53
hydroxide 39, 390
hydrolysis 61, 134
hydronium ion 158
hydrazine 238
hydrazoic acid 239
hydroxylamine 237
hydrolith 182
hydrocarbon 330
hydrochloric acid 291
hydrogen 180
  position of- 171
  occlusion of- 182
  nascent- 183
  atomic- 185
hydrogenite 185.
hydrone 187
hydrogen peroxide 212
  -sulphide 300
hygroscopic subs. 57
hyperol 214
hypochlorite 265, 281
high test- 283
iatro chemistry 5
Iceland spar 415
ignition point 347
indicator 522
incandescence 346
indestructibility
  of matter 11
inert gas 495
Indian red 478
intrinsic energy 142
invar 476
iodate 287, iodide 280

iodometry 271, 315, 538
iodine 270
  -tincture of 273
ion 121, ionic theory 122
ionisation 122, 137
ironac 476
iron, -pyrite 470
  passive- 477
isobar 159
isotope 158
isomerism 60, 75
isomorphism 99
isotonic solution 110
ivory black 320
Jena glass 382
kainite 407, 412
kalium 24
kaolin 379, 433
kelp 271, kiln 387
kieselguhr 378
kieserite 412
kinetic theory 67
kipp's apparatus 188
kohinoor 317
krypton 495
lamp black 321
lanarkite 446
Landolt expt. 14
Lavoisier 1, 6, 224
lanthanide 164
Lane process 187
lapis lazuli 440
laughing gas 240
lead, -ochre 446
  -chamber 307
  -tree 449
  white 451
leadhillite 446
Lebalnc process 401
Le Chatelier principle 117
lignite 321
lime 416, -water 417
  quick-, slaked- 416
  soda- 418, -stone 415
  -light 175
  milk of- 417
  superphosphate of 365
limonite 470
Liebig condenser 48
liquid 8, litmus 522
lixiviation 60
liquation 442
lithopone 420, 525
litharge 449
liver of sulphur 299
lone pair 158
Lother Meyer curve 167
Lowig process 406
Luce Rozan process 462
luminosity of flame 349
lunar caustic 466
magnesia 413, -alba 414
  mixture 363
magnelium 413
magnesite 412
magnesium 412
magnetite 470
malachite 453
manganite 490
manganin 490
manganese 490
  -bronze 490
marble 415
marcasite 480
marsh gas 330
Marsh's test 368
mass, conservation of- 12
mass action, law of 115
massicot 449
match 365, matter 8, 12
matlokite 446
matle 454, matrix 386
matte 454
maxochlor 283
mechanical mixture 18
melaconite 453
melting point 9
metal 20, 385
metallurgy 385
metathesis 60
Mendeleef 162
mercury 428
methyl orange 522
methane 330
mica 379
microcosmic salt 362, 378
milk of lime 417
  -sulphur 298
millerite 483
Millon's base 431
mixture 18
mineral 385
minium 449
mitsch metal 476
Mitschlerich law 99
mispickel 366
mixed crystal 99
Mohr salt 480
Moh's scale of hardness 318
mole 100
molar volume 86, 88
molar solution 525
  -gas constant 65
molecule 22, 83
molecular formula 502
Mond gas 344, -process 483
monel metal 457, 483
monazite 497
mortar 45, 417
mosaic gold 445
mother liquor 55
muffle 387, 401
multiple proportion,
  law of 77
N. Avogadro number 87, 10
nascent state, 183
natural gas 330
natron 395, natrium 24
Nelson cell 399
neon 497
Nessler reagent 431
neutralisation 131, 521
neutron 153
niccolite 483
nichrome 487
nickel, -bloom 483
  -glance, -carbonyl 483
nitrates 391
nitre 407, 409
...-cake 253, -oven 308
nitriding 475
nitrites 246
nitric oxide 241
nitric acid 248
nitrous oxide 240
nitrosyl chloride 252
nitrogen 219
  -cycle 227
fixation of 227
nitrolim 220, 234
Nobel's oil 249
nomenclature 29
non-metal 20
normal density 66
  -solution 523
  temp. and pr. 66
normality 525
nucleus 153
octave, law of 162
occlusion 182
oil gas 344, ochre 478
oil of vitriol 307
oil floatation 386, 454
olefinat gas 333
oleum 307, 312
olevine 412
opal 378
open hearth process 474
orpiment 366
orthoclase 407, 433
ore 385, -dressing 386
osmotic pressure 108
Ostwald process 253
overgrowth crystal 99
oxidation 207
oxidising agent 209
oxide 175, 390
  types of- 175, 176
oxy-acetylene blowpipe 175
  -hydrogen blowpipe 175
oxygen 172, 224
oxone 398, ozone 202
ozonide 204 ...
Parkes process 462

paraffin 332
partial pressure 66
parting 463
passivity 477
Pattinson process 461
pearl ash 408
peat 321
pentlandite 483
perhydrol 213
peroxide 176
perchloron 283
permutit 192
periodic law 162
  -classification 162
permanganate 493
pewter 443, 449
phenolphthalein 522
phlogiston 6
Pharaoh serpent 11
philosopher's wool 421
  -stone 5
phosgne 328
phosphine 357
phosphate 361
photography 464
phosphor bronze 457
phosphorescence 355
physical change 9, 22
phosphoretted hydrogen 357
phosphorite 353
phosphorus 353
  allotrophy of- 355
  -dihydride 355
  -oxychloride 360
photosynthesis 325
pink salt 445
pig iron 472
pitchblende 160
plaster of Paris 419
platnerite 446
platinite 476
plumbum 24
plumbago 318
poling 442, 455
polybasic, -protic 132
  -oxide 176
  -morphism 207
  -halite 407
porcelain 383
position of hydrogen 171
positive rays 151
positron 153
pot ash 407
potash 408
  -alum 439
  -felspar 407
potassium 407
  -bromide 279
  -chlorate 284
  cyanide 409
  -iodide 280
  -dichromate 489
  -permanganate 493
  -perchlorate 285
  -ferrocyanide 481
  -ferricyanide 481
pottery 383, proton 152
Precht process 408
producer gas 343
precipitation 61
Prussian blue 481
promoter 146
proportion, equivalent 78
  fixed -75, multiple -77
Prout hypothesis 6
puddling process 472
purple of Cassias 468
pyrargyrite 461
pyromorphite 446
pyrolusite 490
pyrene 346
pyrex glass 382
pyrite, copper 453, iron-470
pyrogallate 175
quartation 468
quartz 378, -glass 379
quick lime 416
  -silver 429
radical 28
radioactivity 160
artificial 161
Raoult's law 110
rare gas 495
  -earth 164
real gar 366
reciprocal proportion, law of- 78
red copper ore 433
  lead 449, -ochre 478
  -zinc ore 421
  -haematite 470
  -prussiate of potash 481
redox equation 540
reduction 208, 386
reducing agent 209
Reinsh test 367
relative density 85, 498
retort 48
reverberatory furnace 387
reversible reaction 114
respiration 223
Rinman green 424
ring test 251
rock crystal 379
  -salt 406
roll sulphur 296
roasting 386
Rose metal 370
rough 478, rust 476
ruby 433, 437
Saffioni 374
safety lamp 347
sal ammoniac 236
  -volatile 237
salt 37, 132
  types of- 38, 132
  double- 133
  complex- 133
  common 406
saltpetre 219, 409
salt cake 401
sand 378
sapphire 433
satin spar 419
sajimati 395
saturated solution 44
Scheele's green 368
schonite 409
seawater 189
sedimentation 41
Seltzer water 189
self-reduction 388, 447, 455
semi-polar bond 157
  permeable membrane 108
separating funnel 47
Serpeck process 435
serpentine 412
sherardising 424
siderite 470
silica 378
  -glass, -gel 379
  -garden 380
silicate 379
silicol process 185
silicon 376
  -dioxide 378
  -bronze 457
silent electric discharge 202
Siemens' ozoniser 202
silver, -glance 461
  -copper glance 461
  -nitrate, -coin 466
  -mirror, -plating 464
slag 387, 472
  basic- 474
smalt 482
smaltite 482, 483
smelting 386
smithsonite 421
soda, caustic 398
  -lime 418
  washing- 401
  -ash 401, 405
sodamide 395
soda crystals 401
  concentrated- 405
sodium 395
  -amalgam 397
  -cyanide 410
  -peroxide 397
  -hydroxide 398
  -carbonate 400
  -cobaltinitrite 483

  -thiosulphate 314
solder 443, 449
solid 8, sol 147
solubility 44
  -curve 46
  -product 137
solvent, solute 40
solution 40, 44
Solvay process 402
sombrerite 353
soot 316, 321
Sorel cement 415
spathic iron ore 470
spathose 470
specific gravity 498
speiss cobalt 482
spelter 422
spent iron oxide 343
  -lime 343
spinel 433
spiegeleisen 474, 490
spitting of silver 464
stalactite 191
stalagmite 191
standard soln. 523
stannum 24
stannous chloride 444
stannic chloride 444
stannite 444
Stassfurt deposit 407
steam oven 58
steel 473
  varieties of- 475, 476
  high speed tool- 476
  stainless- 476
stellite 482
stibine, stibnite 369
stibium 24
stoichiometry, laws of 75
stromeyerite 461
strontianite 419
strontium 419
structural formula 28
sugar charcoal 319
  -of lead 449
sulphates 329
sulphides 392
sublimation 51
suspension 47
superphosphate 365
sulphur, roll- 295
  flowers of- 295
  alltropy of- 295, 298
  -dioxide 303
  -trioxide 307
sulphuretted hydrogen 300
sulphuryl chloride 314
sylvine 263
symbol 24
synthesis 60
sympathetic ink 54, 482
talc 379, 412
tantiron 476
tar, wood- 319
  coal- 342
tartar emetic 370
tempering 475
tenorite 453
tetramethyl base 205
Thenard blue 440
thermit 436
thermochemistry 142
thionyl chloride 306
Thomas slag 474
  -Gilchrist process 474
tin, -stone, 441
  :plague, -plate 443
tinning 443
tincal 373
tincture 41
titration 522
topaz 435
tourmaline 433
transition temp. 297
  -element 163
transmutation 5
trona 395, -artificial 161
tridymite 378
tritium 158
tuyeres 471
Turnbull blue 481
turquoise 433
Tyndall effect 149
type metal 369, 449
ulexite 373
unsaturated soln. 44
valency 26, 156
vapour density 85, 1
  abnormal- 118
vaporisation 9
Venetian red 478
vermillion 432
Victor Meyer method
vitreosil 379
vivianite 383
vitriol, blue- 459
green- 480
  oil of- 307
  white- 425
voltameter 11
volume strength 216
  atomic- 167
vycor 379
washing soda 401, 405
wash bottle 49
water 188, -bath 40
  electrolysis of- 11
  natural- 188
  hard and soft- 189
  drinking- 194
  -softening 190
water gas 185, 343
  semi- 344
wavelite 353
weathering of rocks 226
Weldon process 266
white lead 451
  -vitriol 425
  -arsenic 367
willemite 214
witherite 419
wolfram 24
wolframite 441
Wood's metal 427
wrought iron 472
wulfenite 446
xenon 495
y-alloy 437
yellow ammonium sulphi
  phide 237
  -prussiate of potash 481
zeolite 192
zinc, -blende 421
zincite 421